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ABSTRACT

M.Sc. Chemistry

William James Brickman

MODIFICATIONS IN CELLULOSE ACCESSIBILITY

DUE TO

REPEATED WETTING AND DRYING

This thesis is concerned with the modifications brought about in cotton linters by varying their moisture history. It has been shown that wetting with distilled water, followed by drying over phosphoric anhydride under vacuum, when repeated up to twenty-five cycles, brings about a gradual increase in the accessibility of the linters to thallous ethylate. This increased accessibility is paralleled by a correspondingly greater ease of nitration. Confirmation of these trends of changing accessibility of cotton linters was obtained from the results of hydrogen - deuterium exchange reactions. There was no indication, over the complete twenty-five cycles, that a maximum accessibility had been obtained.

Increasing the temperature of the distilled water for the immersion to approximately 80°C. for a series of six wetting and drying cycles brought about a decrease in the accessibility of the dried linters to thallous ethylate. Methods of manipulating and storing cotton linters appear to exert an influence on the accessibility.

THE UNIVERSITY OF ALBERTA

MODIFICATIONS IN CELLULOSE ACCESSIBILITY DUE TO REPEATED WETTING AND DRYING

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

FACULTY OF ARTS AND SCIENCE

DEPARTMENT OF CHEMISTRY

by

W. JAMES BRICKMAN, B.Sc.

EDMONTON, ALBERTA,

APRIL, 1951.

Thesis
1951
6

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ERRATA

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Item B. IV "(c) Moisture Equilibrium Correction" should read, "(c) Correction for Moisture Absorption".

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Figure 13, After "....in Tables IV and IX" insert, "(Samples I-10A, S-I, S-II, S-III, S-IV, S-V, C-I)"

Introduction

Page 3, line 8, "....substances and hence experiencing least..." should read, "....substances, hence experiencing least...".

Page 10, line 6 "...are shipped after removal on steam heated cylinders of from 70 to 90 per cent of the water, a condition..." should read "...are shipped, after removal on steam heated cylinders of from 70 to 90 per cent of the water, in a condition..."

Page 13, line 19, "...by refluxing with.....in a receiver solution..." should read "...by refluxing in hydriodic acid (41,42) and then collected as methyl iodide in a receiver solution...".

Page 15, line 16, "By far the simplest.....nitrometer (52)." should read, "A du Pont semi-micro nitrometer (52) was found to provide the simplest and quickest method of nitrogen estimation."

Experimental

Page 35, line 1, should read "75 - 100 ml. of liquid was distilled..."

Discussion and Results

Page 79, line 23, should read, "...had been first mercerized with the same strength..."

Bibliography

Page 83, ref. 6, include "1st Ed."

ref. 7, include "1st Ed."

ref. 10, include "2nd Ed."

Page 85, ref. 43, include "New Ed."

Page 86, ref. 54, include "2nd Ed."

ref. 62, include "1st Ed."

ref. 65, include "3rd Ed."

Page 87, ref.70, include "1st Ed."

General

Substitute "desiccator" for "dessicator" and "per cent" for "percent" where they occur as such.

GENERAL INTRODUCTION

The discovery of the unreliable nature of the burning properties of nitrocellulose obtained from North American pulps has accelerated investigations into the causes of these irregularities (1). Brown and Purves (2) have shown that two samples of cellulose differing only in their moisture history showed quite different degrees of nitration when treated with the same nitration mixture. Thus, the nitration of highly swollen cotton linters, first wetted with water and dried directly, yielded a product of lower nitrogen content than that obtained from identical nitration of the swollen linters which had not been wetted and dried. It was thought that the removal of water during the drying process "collapsed" the linters and produced a cellulose with at least some regions less readily penetrated by the nitration mixture. Continuing this line of research, Rosenthal and Brown (3) subjected dewaxed cotton linters to a series of wetting and drying cycles using distilled water as the wetting and swelling medium (rather than the caustic soda solution employed by Brown and Purves). The dried samples taken after each cycle, when nitrated with a standard nitration mixture, exhibited a small but significant increase in extent of nitration paralleling the increase in number of wetting and drying cycles. The major portion of the increase ($\sim$0.4%) appeared to occur between cycles 1 to 9, but no definite indication of a maximum nitrogen value was obtained with linters receiving up to 17 cyclic treatments. It was suggested that the increase in ease of nitration on wetting and drying the linters several times might be due to a change in the physical structure of the linters, facilitating penetration of the reagent.

The purpose of this research was to establish, if possible, by extending the number of wetting-drying cycles, the point at which maximum nitration can be obtained. The effect, upon the changes in extent of nitration, of higher temperatures of the swelling liquid, and of variations in mechanical manipulation of the samples was also to be considered. It was hoped also that from the data accumulated, some insight might be obtained concerning the fundamental causes of the peculiarities observed.

The deuterium - hydrogen exchange technique of Frilette, Hanle and Mark, (4) was also to be employed as a method of measuring the degree of accessibility of linters samples chosen after appropriate numbers of cycles, with the hope that they would show numerical differences larger than those found by the thallation technique of Assaf, Haas, and Purves (5), and also bear out the results obtained from nitrations of the linter samples.

HISTORICAL INTRODUCTION

Cellulose is an important constituent in most vegetable structures. Since this is an abundant raw material which is steadily replenished by nature, detailed knowledge of its characteristics is important. In its natural state, cellulose is accompanied by non-cellulosic materials, lignins, fats, waxes, etc., which must be removed. Since cotton fibers contain the lowest percentage of non-cellulosic materials (from 3 to 15%) (6), they require less drastic treatment to remove interfering substances and hence experiencing least disturbance of the cellulose macromolecule. Accordingly, most detailed study has been confined to cellulose from cotton fibers. The seed hairs on cotton fall into two classes, lint and fuzz fibers, more commonly called cotton and cotton linters respectively. Cotton or lint, is used widely in the textile industry. The short fuzzy fibers or cotton linters, are used where the length of the fiber is not important, such as in the manufacture of regenerated cellulose or rayon products, or in the production of nitrated or acylated derivatives. Cotton linters, in the conditions that we receive them, consist largely of α-cellulose, technically defined as that portion which is insoluble in 17 to 18 percent cold alkali. Pretreatment had been given to remove the hemicelluloses which included the β-cellulose and the γ-cellulose (7).

Technically, "cellulose" denotes the residues obtained by subjecting vegetable materials to certain pulping processes (8). Chemically speaking, "cellulose" is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies. Over a century of research has yielded a structure which agrees with all the known chemical properties of cellulose (Fig.3). It consists

of glucose anhydride units (usually over 1000) joined through the 1 and 4 carbon atoms with a β-glucosidal linkage (Fig.3) (8). The chief degradation end products are glucose (Fig.1) and cellobiose (Fig.2) (9,10). The macromolecules are known to vary considerably in length even in the same sample of cellulose. The length of these chains is measured in terms of "degree of polymerization" (abbreviated D.P.) which represents the average value for the number of glucose anhydride units in the cellulose molecule. For example, the D.P. for cotton lint is 2020, while that for cotton linters is 1440 (11). A partial hydrolysis can lower this to the 50 - 500 range without the naked eye detecting a change in appearance.

The physical properties of cellulose are generally those expected of a long chain polymeric substance. Much investigation, particularly by the powerful method of X-ray analysis, has led to the conclusion that cellulose is composed of crystalline and non-crystalline areas (Fig.4) (12). Crystalline areas are believed to be regions where adjacent macromolecules are sufficiently close together to allow neighboring hydroxy groups to exert an influence on bonding of the adjacent chains. The rearrangement of hydroxyls and the cellulose chains in order to give the greatest satisfaction of these forces brings about a certain alignment which produces a crystal lattice. Between these areas of order exist regions which are in a more or less disordered state. These are often termed the "amorphous" portion of the cellulose. Nickerson (13) has produced evidence which indicates the existence of a "mesomorphous" region - one whose state of order is intermediate between that of the crystalline and definitely non-crystalline cellulose.

Below the age of five days, cotton hairs give no evidence

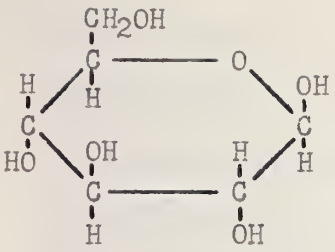


Fig. 1 β-Glucose

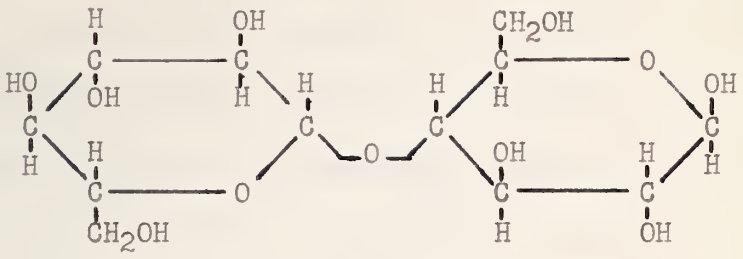


Fig.2 β-Cellobiose

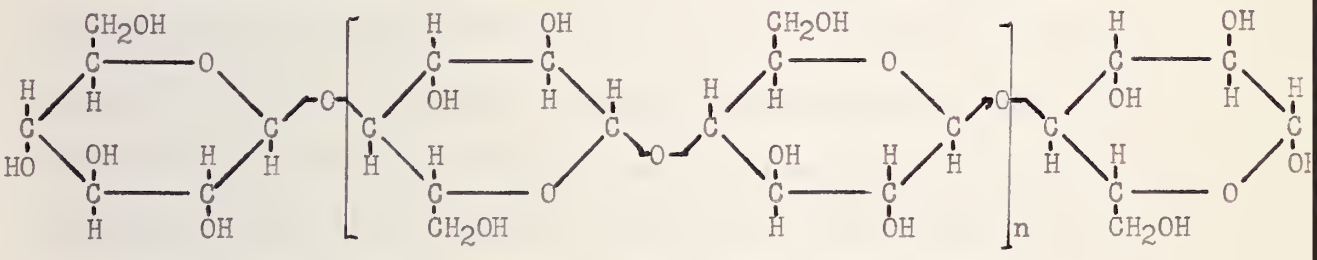


Fig.3 Plane projection of cellulose chain and its constituent units

Fig.4 Arrangement of chain molecules in cellulose. Heavy lines constitute the crystalline regions, fine lines are the amorphous portions.

of crystallinity (14), but after this age, crystallinity is detected by X-ray characteristic Laue patterns or the property of double refraction (15). The mature fiber is largely crystalline in nature. This has been confirmed by measurements of accessibility to thallous ethylate which indicates a non-crystallinity of less than one percent (5). Urquhart (16) has suggested an explanation for this phenomenon. When cellulose is formed inside the cotton hair, it is precipitated in the presence of water and the hydroxyl groups accordingly have molecules of water attached. As water is removed and the hair dries, these hydroxyl groups will be freed, and it is reasonable to assume that there will be a tendency for the cellulose molecules to rearrange themselves so that the residual (secondary) valences of the hydroxyl groups will be mutually satisfied. When this commences, the submicroscopic crystals are grouped to form crystallites (or crystalline areas) which give a characteristic X-ray pattern (17). This process presumably continues during the drying of the cotton until all the absorbed water has been removed. In addition to the rearrangement of the molecules in the micelles (minute cells), some deformation (twisting) of the micelles themselves may occur and assist in bringing free hydroxyl groups nearer to each other. It is not assumed that the rearrangement always does occur. It is probable that some macromolecules will be held more rigidly than others, and it may be that a change in arrangement is possible only with those loosely bound molecules which attain momentarily a sufficiently large amplitude of vibration. Thus, even in the dry condition there will be a large number of free active groups on the micellar surfaces not involved in hydrogen bonding or crystallite formation.

Nageli (18) pictured the plant structure of cellulose to consist of minute cells which he termed micelles, separated by spaces referred to as intermicellar spaces. Studies show that many reactions proceed more easily in the regions between fibrils (the finest fiber structures) than within the fibrils. Since the crystalline cellulose is located principally within the fibrils, whereas the interfibrillar regions contain in large measure, the amorphous fraction (19), the latter portion of the cellulose is therefore susceptible to reaction. X-ray data of wetted cellulose shows most of the water in the amorphous areas (20). Since the Laue pattern of dry cellulose undergoes no alteration when exposed to water (21), this is an indication that water causes little disturbance of the crystalline areas. Katz (22), was the first to show that the spacings of the cellulose X-ray diagram are entirely unchanged by swelling in pure water. In Nageli's terminology, therefore, swelling in pure water is an intermicellar rather than an intramicellar process.

Due to the abundance of hydroxyl groups, cellulose may be expected to possess great attraction for water, but the amount of water taken up by individual cellulose fibers after the system has reached equilibrium is much smaller than that expected on the basis of the number of hydroxyl groups (23). This is explained by assuming that only those hydroxyls on the chain bundle surface are available to the water molecules. It is calculated from X-ray data that 30 - 50% of the total hydroxyls of cellulose are on the surface of micelles (23), the rest being located within the spaces between the individual chains where they are inaccessible to water.

Water molecules are considered to be held to the hydroxyl groups by three main forces (24).

1. Secondary valences, or residual affinity for water of the hydroxyl groups of cellulose.

2. Polarity of the hydroxyl groups.

3. Hydrogen bonding.

Stamm and Tarkow (25) state that fibers of pure cellulose and lignocellulosic materials such as wood, can be penetrated directly only by polar liquids which form a solid solution with the fibers. The extent of penetration and swelling is dependant on the ability of the liquid to form hydrogen bonds with the hydroxyl groups of the cellulose and the lignin, and also on the size of the liquid molecules.

Several swelling theories have been advanced which are concerned with the penetration by, or absorption of, a swelling medium by a swelling solid (26). These are discussed in some detail by Stamm (27) and are summarized as follows.

1. The absorbed ions from a solution of an electrolyte, together with the immobilized ions of opposite charge which remain in close proximity to the absorbed ions, bring their sphere of water with them. This water hydration of the ions is thought to be responsible for the swelling of the solid.

2. The electrical charge set up on the surface due to selective absorption of ions or molecules, results in a repulsion of the like surface charges which allows water to enter mechanically. This theory is applicable to water, dilute aqueous solutions and non-dissociated organic liquids, but not to concentrated aqueous solutions of electrolytes.

3. A Donnan membrane equilibrium is set up which results in a higher concentration within the membrane than on the outside and a subsequent taking up of water by osmosis due to

concentration differences. This theory assumes the presence of diffusible electrolytes in solution and an appreciable ionization constant of the swelling material. The lyotropic series has been found to apply (27).

Aqueous solutions, employed as swelling media, greatly increase the diameter of the fiber. According to Dorée (28) this is accompanied by a slight decrease in fiber length. However, more recent reports claim that the length of the swollen fiber has also suffered and increased, though only to the extent of about 1.1% (29).

It is interesting to note that a hysteresis effect has been observed when moisture is absorbed and removed from cellulose (30). During the desorption the amount of water retained by the cellulose is found to be greater than that which the fully dried cellulose can reabsorb under the same conditions. Urquhart (31) has offered an explanation to account for this behaviour. 'After complete desorption of water, if the cellulose is exposed to water, the absorption will take place first at the free active hydroxyl groups on the micellar surfaces (16). The absorbed water will by its attraction tend to restore the original orientation of the surface so that during absorption the number of active groups will increase. This increase, however, will yield an "accessible" surface somewhat less than that present prior to desorption to the dry state, since the amplitude of vibration of a macromolecule held to another by the attraction of one or more hydroxyl groups will be less than that of a molecule with these active groups free. Thus there will be less tendency for a hydroxyl group to return to the surface than there was originally for it to leave the surface. Hence the absorbing surface will be in a less

active condition during the absorption than during the prior desorption, and hysteresis will result. Repeated immersions in water and subsequently drying might conceivably behave in a similar manner.

Drying of a swollen or wetted cellulose has an effect on the properties of the cellulose. Most purchased pulps (excluding groundwood) are shipped after removal on steam heated cyclinders of from 70 to 90 per cent of the water, a condition technically termed as "air-dried". In the subsequent beating processes, the fibers are saturated with water with consequent swelling and softening. The fibers swell in the water at a rate which is somewhat dependant, inversely, on the extent to which they had previously been dried (31). Therefore in paper making, a longer beating period is required for pulps that have been dried.

Jayme (32) observed that the drying of the pulp resulted in an irreversible process which he termed "hornification". He found the decreased ability of the dried cellulose to reabsorb and retain water was related to the severity of drying conditions. This effect he attributed to the hemicellulose remaining on the cellulose fibers. The fibers, collapsed in the capillary and porous areas by water removal, were held together by forces of adhesion and cohesion. In subsequent wetting, these areas are inaccessible to water and hence papermaking qualities are decreased.

The temperature of the aqueous wetting and swelling solutions is reported to affect the degree to which cellulose can be swollen. A 5% solution of caustic soda has a greater swelling effect at 0°C. than a 20-30% solution at 70 - 80°C. (33). This difference is explained on the basis of the size of the water envelope carried by the cation. At lower temperatures the cations are able to carry larger water shells

than at higher temperatures, hence a lower degree of swelling occurs at higher temperatures (34).

Mercerized cellulose, i.e. cellulose which has been swollen with caustic soda, washed, and dried, normally possesses greater hygroscopicity than the normal cellulose. This ability seems to be lost if the alkali is washed out with boiling water (35), which is probably due to the tendency of the mercerized cellulose to revert to its natural modification under such treatment. This is borne out by the fact that the X-ray pattern changes to a considerable extent to that of unmercerized cellulose (36).

Successive cycles of swelling with distilled water, followed by removal of the water under vacuum over a strong dessication agent such as phosphoric anhydride, has been shown to produce a series of cellulose samples which exhibit an increasing ease of nitration (3), as well as small but apparently significantly increasing accessibility to thallous ethylate in ether paralleling the number of wetting and drying cycles. This is in sharp contrast to the usual decrease in water sorption or reactivity reported for the dried cellulose. To account for this, each cycle may be compared to the action of a zipper. During the wetting with water, the hydroxyls, held together by mutual attraction, become separated by water molecules. Drying removes this water, causing the cellulose molecules to undergo rearrangements again to satisfy secondary valences and close the "zipper". Repeating this has an effect, it might be said, similar to that found in the wearing of the zipper, each successive wetting increases the number of hydroxyls readily available for reaction after drying has occurred.

Until recently, the terms accessibility, non-crystallinity,

and amorphous cellulose, have been used interchangeably. This does not present a true picture, since the accessibility is a function of the reagent used in its determination. Hence one should express the accessibility of cellulose in terms of the reagent and concentrations of reagents used.(37).

It can be seen that the measurement of the accessibility of cellulose is of considerable value in evaluating the properties of cellulose from different sources. A number of reagents have been used with varying degrees of success to measure accessibilities. Nickerson (38) showed that the initial rapid hydrolysis and oxidations of various celluloses can be attributed to the more accessible portion. Goldfinger, Siggia, and Mark (39), found the reaction of cellulose with periodic acid took two stages which they considered to be a measure of the more easily accessible and less accessible portions. Brown and Purves (2) employed nitration under standard conditions as a means of evaluating accessibilities to nitrating mixtures. Furthermore, Frilette, Hanle, and Mark (4), used hydrogen - deuterium exchange to get an empirical value for total accessibility and an approximate estimate of the crystallinity. Nickerson (37) has recently referred to determining accessibility by employing formic acid, but as yet no details have been published. It is significant to note that all these methods also bring about swelling during the process, therefore they do not give an estimation of the actual accessibility before reaction with the reagents. The method of Assaf, Haas, and Purves (40), using an ethereal solution of thallous ethylate, is designed to measure only those areas which in the dry state can be penetrated by a non-polar organic solvent. Its chief advantage is that no swelling is produced during the determination.

The present investigation makes use of only three of these methods, thallation and methoxyl estimation, nitration, and heavy water exchange. The heavy water exchange was attempted in an effort to supplement and confirm the results of the other two methods.

In excess of two hundred thallation and methoxyl determinations were run in measuring the accessibility in the dry state of samples of cotton linters. For these determinations, the thallous ethylate was prepared according to the equation,

$$2\ Tl + 2\ EtOH \rightarrow TlOEt + H_2$$

This thallous ethylate was used in ether solution to react with the cellulose hydroxyls forming thallous cellulosates,

$$TlOEt + Cellulose\text{-}OH \rightarrow Cellulose\text{-}OTl + EtOH$$

with only those hydroxyls accessible to the non-polar solvent. The methylation step was accomplished with methyl iodide.

$$Cellulose\text{-}OTl + CH_3I \rightarrow Cellulose\text{-}OCH_3 + TlI.$$

Methoxyl substitution of the partly methylated cellulose thus gives a measure of the number of hydroxyls which came in contact with (accessible to) the ether solution of thallous ethylate. The methoxyl groups were split off by refluxing with hydriodic acid (41,42) and collecting the methyl iodide formed in a receiver solution containing bromine.

$$Cellulose\text{-}OCH_3 + HI \rightarrow CH_3I + Cellulose\text{-}OH$$

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

Excess bromine then oxidized the iodine bromide to iodic acid,

$$IBr + 2\ Br_2 + 3\ H_2O \rightarrow HIO_3 + 5\ HBr$$

and when this had occurred, the excess bromine was destroyed with formic acid. This reaction is facilitated by the presence of the iodine compound to act as a carrier.

$$Br_2 + HCOOH \rightarrow 2\ HBr + CO_2$$

The determination was completed by normal analytical methods (43) for iodine using standard sodium thiosulfate and starch indicator.

$$HIO_3 + 5\ KI + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow S_4O_6^{=} + 2\ I^- + 4\ Na^+$$

Since six equivalents of iodine were liberated for each methoxyl, it was possible to determine small quantities of methoxyl.

Degree of nitration was chosen as a method to evaluate the reactivity of cellulose (44,45). Nitrations may be carried out by a number of different methods, as has been pointed out by Rosenthal (46), but the laboratory procedure chosen was one usually employed in commercial nitrations. Initially a large stock supply of an analyzed technical nitration mixture was prepared which would produce a nitrocellulose containing approximately eleven per cent nitrogen (47). Careful repetition of technique in nitration, washing and stabilizing resulted in an uniform product freed from the danger of spontaneous decomposition due to impurities. The formation of the nitrate ester may be represented as,

$$\text{Cellulose-OH} + HNO_3 \rightarrow \text{Cellulose-}ONO_2 + H_2O$$

The product, called a nitrate, is really the ester of nitric acid with the alcohol groups on cellulose.

Two methods of analysis were used to determine the nitrogen content of the samples. The modified semi-micro Kjeldahl procedure employed by Brown (2) can be summarized with the following equations (48).

$$2\ \text{Cellulose-}NO_3 + H_2SO_4 \leftrightarrows (\text{Cellulose})_2SO_4 + 2\ HNO_3$$

$$2\ HNO_3 + 2\ C_6H_4\cdot OH\cdot COOH \rightarrow 2\ C_6H_3\cdot OH\cdot NO_2\cdot COOH + 2\ H_2O$$

$$6\ Na_2S_2O_3 + 6\ H_2SO_4 \rightarrow 6\ Na_2SO_4 + 6\ H_2SO_3 + 6\ S$$

$$6\ H_2SO_3 + 2\ C_6H_3\cdot OH\cdot NO_2\cdot COOH + 2\ H_2O \rightarrow$$

$$\rightarrow \quad 6\ H_2SO_4 \ + \ 2\ C_6H_3.OH.NH_2.COOH$$

A trace of selenium, as a catalyst (49), and potassium sulfate to raise boiling point, were added before digestion.

$$2\ C_6H_3.OH.NH_2.COOH \ + \ 27\ H_2SO_4$$
$$\rightarrow \quad (NH_4)_2SO_4 \ + \ 14\ CO_2 \ + \ 26\ SO_2 \ + \ 30\ H_2O$$
$$6\ S \ + \ 12\ H_2SO_4 \ \rightarrow \ 18\ SO_2 \ + \ 12\ H_2O$$

The cooled, diluted and basified solution was distilled into boric acid containing a special indicator (50).

$$(NH_4)_2SO_4 \ + \ 2\ NaOH \ \rightarrow \ 2\ NH_3 \ + \ 2\ H_2O \ + \ Na_2SO_4$$

The ammonia in the boric acid solution was titrated with standard dilute hydrochloric acid.

The method of Marcali and Rieman (51) which omitted the distillation step and used direct titration with two different indicators was tried. The results were not sufficiently accurate to warrant further use.

By far the simplest and quickest method of nitrogen estimation was found to be using a du Pont semi-micro nitrometer (52). The nitrogen content was calculated from the volume of nitric oxide liberated on the reaction of the nitrocellulose with concentrated sulfuric acid in the presence of mercury.

$$Cellulose\text{-}ONO_2 \ + \ H_2SO_4 \ + \ Hg$$
$$\rightarrow \quad Cellulose\text{-}OH \ + \ NO \ + \ H_2O \ + \ HgSO_4$$

Since Frilette, Hanle, and Mark (4), by the heavy water exchange technique reported an accessibility of forty-six per cent for linters, it was hoped that the very small differences between the samples of wetted and dried linters, as shown by thallous ethylate accessibility measurements, would be proportionally larger. The accessibility determination involves the exchange of deuteriums for

hydrogens on the cellulose hydroxyls.

$$\text{Cellulose-OH} + D_2O \rightarrow \text{Cellulose-OD} + HOD$$

Therefore the progress of the reaction could be followed by extracting samples of heavy water at regularly timed intervals and measuring their densities. The densities of successive samples showed a decrease due to the replaced hydrogens diluting the heavy water. An empirical factor based on these densities was plotted against the time of reaction to give a curve for each cellulose sample. The relative slope and height of the curve was used as a measure of the accessibility of the sample to a known deuterium oxide concentration.

EXPERIMENTAL

A. Preparation of Cellulose Samples

A quantity of high grade cotton linters, donated by H.M. Spurlin and the Hercules Powder Co., was dewaxed by extraction for 48 hours in a 1500 ml. Soxhlet apparatus, with a mixture of two parts benzene and one part ethanol. The linters were then dried in air and subsequently stored in a large closed container until needed.

I. Swelling of Cellulose Samples with Distilled Water at Room Temperature. Series I and II.

The samples of cellulose were swollen using a modified form of the procedure outlined by Rosenthal (53). One hundred and sixty grams of air-dried, dewaxed cellulose were immersed in distilled water at approximately 26°C. and allowed to soak for three hours, filtered through a large Buchner funnel (with filter paper present to retain the finer fibers) under mild suction. The linters were lightly pressed to remove excess water and dried in a dessicator over phosphoric anhydride, under vacuum. Fresh phosphoric anhydride was added when the surface of the drying agent became liquefied. When on adding fresh phosphoric anhydride and evacuating, there was no evidence of moisture on the surface of the powder, the sample was considered dry. The process was repeated, on the dried linters in order to obtain a series of dried samples which had passed through 0, 1, 5, 9, 13, 17, 21, and 25 wetting and drying cycles. These samples were stored initially over concentrated sulfuric acid, then when creeping of the sulfuric acid was noted on the sides of the dessicator, they were stored over fresh phosphoric anhydride. (Table I)

TABLE I

WETTING CYCLES OF COTTON LINTERS IN DISTILLED WATER - SERIES I

Samples dried over phosphoric anhydride under vacuum.

Stored in the dark at room temperature over phosphoric anhydride.*

Sample	Cycles	Time Immersed at 23-29°C.	Time of Drying Before Next Wetting	Sample Weight Taken
I-0	0	0 hours	0days	20 g.
I-1	1	3	17	20
	2	3	13	
	3	3	10	
	4	3	15	
I-5	5	3	20	20
	6	3	35	
	7	3	16	
	8	3	14	
I-9	9	3	6	15
	10	3	5	
	11	3	7	
	12	3	9	
I-13	13	3	7	15
	14	3	7	
	15	3	7	
	16	3	6	
I-17	17	3	9	15
	18	3	12	
	19#	3	8	
	20	3	7	
I-21	21	3	6	
	22	3	4	
	23	3	4	
	24	3	4	
I-25	25	3		15

* All samples up to cycle 25 were stored in one dessicator over concentrated sulfuric acid until completion of cycle 25. They were then all transferred to vacuum dessicators and stored under mild vacuum over phosphoric anhydride.

Temperature on wetting 19 accidentally rose to about 70°C. during heating.

TABLE II

WETTING CYCLES OF COTTON LINTERS IN DISTILLED WATER - SERIES II

Samples dried over phosphoric anhydride under vacuum.*

Stored in the dark at room temperature over phosphoric anhydride.

Sample	Cycles	Time Immersed at 23-29°C.	Time of Drying Before Next Wetting	Sample Weight
II-0	0	0 hours	0 days	10 g.
II-1	1	3	13	10
	2	3	8	
	3	3	8	
	4	3	7	
II-5	5	3	8	10
	6	3	10	
	7	3	7	
	8	3	10	
II-9	9	3	8	10
	10	3	6	
	11	3	8	
	12	3	10	
II-13	13	3	10	10
	14	3	11	
	15	3	7	
	16	3	8	
II-17	17	3	7	10
	18	3	3	
	19	3	3	
	20	3	3	
II-21	21	3	3	10
	22	3	3	
	23	3	3	
	24	3	4	
II-25	25	3		10

* Drying was slightly different from Series I. No initial air drying and no pressing of linters to remove excess moisture. On completion of drying, samples of linters were immediately stored over phosphoric anhydride under mild vacuum.

II. Swelling of Cellulose Samples with Distilled Water at Approximately 70 - 90°C. Series HT.

The linters were immersed in distilled water brought to 70 - 90°C. on a steam cone, allowed to soak three hours at this temperature, then filtered through a large Buchner funnel (using a filter paper to retain the fine fibers) under mild suction and lightly pressed to remove excess water. They were then dried over phosphoric anhydride under vacuum in a dessicator. The process was repeated on the dried linters and samples taken at 0, 3, and 6 cycles. These dried samples were stored over fresh phosphoric anhydride. (Table III)

TABLE III

HIGH TEMPERATURE WETTING CYCLES OF COTTON LINTERS IN DISTILLED WATER AT 70 to 90°C. SERIES HT

Samples dried over phosphoric anhydride under vacuum and stored at room temperature over phosphoric anhydride in the dark.

Sample	Cycles	Time Immersed at approx. 80°C.	Time of Drying Before Next Wetting	Sample Weight
HT-0	0	0 hours	0 days	5 g.
	1	3	11	
	2	3	32	
HT-3	3	3	36	2
	4	3	16	
	5	3	14	
HT-6	6	3		7

III. Solvent Exchange Drying

A five-gram sample of dewaxed linters which had been immersed for the usual three hour period, was filtered and the excess water gently pressed out, then this was quickly dispersed and stirred in 250 ml. of 99% methanol. Fifteen minutes later, this methanol was replaced. After five such washings, the linters were then immersed in magnesium-dried methanol for two washings of thirty minutes each, using 250 ml. volumes as above. The alcohol was removed by filtration and the linters were then immersed for 30 minutes in 250 ml. of sodium-dried, thiophene-free benzene. Then followed three more such washings for fifteen minute periods each, to remove the last traces of the methanol. The linters were then dried in a vacuum dessicator over solid paraffin wax and phosphoric anhydride, whereupon the samples were stored over phosphoric anhydride together with the other samples of Series I.

The reagents were recovered and purified.

IV. Extended Exposure of Samples to Atmospheric Conditions

Samples of cellulose from each of the Series I cycles, 0, 1,5,13,17,21, and 25, were stored in a container protected from dust where they could be exposed to atmospheric room conditions in the laboratory office for six months. The large weighing bottles containing these samples were then transferred to a vacuum dessicator and dried over phosphoric anhydride for a month prior to analysis.

V. Mechanical Treatment of Some Linters During Wetting

Two samples of original linters were wetted simultaneously. One sample was continuously stirred at a slow rate for the regular

three hour wetting time. It was then carefully filtered by suction and no pressing of excess moisture was used before drying over phosphoric anhydride. The second sample was given no stirring, the excess moisture being slightly pressed out when filtering in the Buchner funnel. The two samples then were dried over phosphoric anhydride under vacuum. Subsequent storing over phosphoric anhydride under vacuum was in the dark under identical conditions in the same dessicator.

VI. Swelling with Aqueous Sodium Carbonate

A 5-gram sample of cotton linters was immersed for two weeks in a ten per cent solution of sodium carbonate. The sample was freed of liquid by filtration and washed with 250 ml. of distilled water. The linters were then dropped into a mechanically stirred solution of 800 ml. of ten per cent acetic acid. Stirring continued for thirty minutes.

After two washings with distilled water, four with dry methanol, and four with pure, dry benzene, the sample was stored under vacuum over paraffin wax and phosphoric anhydride.

B. Determination of Accessibility of Swollen Cotton Linters

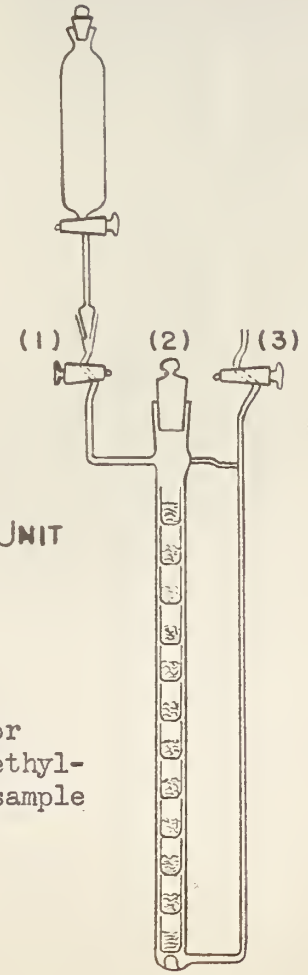
I. Thallation and Methylation of Dry Cotton Linters

The dried cotton linters were thallated and methylated using a slightly modified form of the procedure developed by Purves (5).

Determinations were carried out in triplicate on cotton linter samples of approximately 0.1 gram. The samples were quickly transferred from the dessicator in which they were stored in labelled beakers, into tared, dry cups, rapidly weighed and transferred to the thallation unit (Fig.5). Stopper 2 was quickly replaced and the unit evacuated to a pressure of approximately one millimetre with an oil pump attached to 3, in order to remove excess atmospheric moisture and facilitate penetration by the solution. Low results are obtained if this evacuation is neglected.

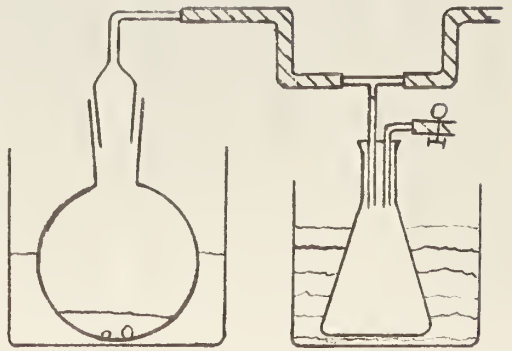
When the samples had been at 1.0 mm. pressure for about ten minutes, stopcock 3 was closed. Stopcock 1 was opened and approximately 60 ml. of 0.1N thallous ethylate was sucked in to fill and cover the cups. The apparatus was then allowed to stand in the dark for one hour while thallation proceeded. Thallous ethylate decomposes readily in the presence of light, so exposure to light was limited to a bare minimum. The partially exhausted thallous ethylate was removed by suction (water-pump) through stopcock 3, into a trap. The partially thallated samples were protected from moisture of the water pump by a calcium chloride tube between the trap and the pump. Fresh 0.1N thallous ethylate was again added and the apparatus allowed to stand in the dark for an additional hour.

The thallation solution was then replaced through stopcock 3, by dry thiophene-free benzene. A series of washings with dry, thio-



THALLATION UNIT

Fig.5 Apparatus used for thallation and methylation of twelve sample cups.



THALLOUS ETHYLATE PREPARATION

Fig.6 Apparatus used in distilling off the excess ethanol, showing ground-glass adapter and trap used.

phene-free benzene followed, one of fifteen minutes, and four of five minutes duration to remove the thallous ethylate.

The samples thallated in ether were colored yellow, the depth of color being a rough indication of the extent of thallation. Usually samples showing an accessibility below one per cent were quite pale yellow, while those of two to four per cent were a more pronounced yellow.

The samples were prepared for methylation by filling the apparatus with a large excess of methyl iodide in benzene. Approximately 12 ml. of methyl iodide were added along with sufficient dry, thiophene-free benzene to fill the apparatus. No further exclusion of light was necessary after addition of the methyl iodide. The apparatus was left overnight in this state.

The ground glass stopper 2 was replaced with a Tamworth condenser equipped with a calcium chloride tube. Stopcocks 1 and 3 were closed and the apparatus immersed in a 4-liter beaker water bath. The surface of the water was covered with melted paraffin wax to prevent evaporation and to maintain the bath at 80°C. Since it was not possible to completely immerse the apparatus to the level of the top cup, a cover was made to hold the heat in around the upper part of the unit during a three and one half hour reflux period.

The methylation was accompanied by a change in color of the samples from yellow to orange, due to the formation of thallous iodide which remained occluded in the sample. The intensity of color again provided a rough approximation of the amount of accessible cellulose in the sample.

The condenser was then replaced by a glass stopper and the

benzene-methyl iodide mixture was extracted by use of the trap, water-pump system used in previous steps. Fresh, dry, thiophene-free benzene was added to fill the apparatus, allowed to remain in contact with the methylated cellulose for two or three minutes, then removed. This was followed by two additional extractions of fifteen minutes each. Six further extractions of five to ten minutes each were given to complete the removal of the last traces of methyl iodide. Any residual traces of methyl iodide would completely invalidate subsequent methoxyl determinations.

The benzene in turn was removed as thoroughly as possible by water pump. Two hours at 80°C. under a pressure of 1 mm. with the aid of an oil-pump yielded dry, solvent-free, methylated linters.

The samples were now analysed for methoxyl content, the methoxyl content being expressed as a percentage of the original unsubstituted cellulose. Multiplication by the factor 100/57.4 (5), gave the percentage of the cellulose hydroxyl groups that had been methylated. This was assumed to be equal to the percentage of cellulose accessible to thallous ethylate in ether.

Preparation of Thallous Ethylate Solution (5)

A stick of thallium metal was scraped free of crusted oxide to expose the clean, silvery metal. Approximately three to four grams of fine shavings of the clean, silvery metal were placed in seventy-five to one hundred milliliters of absolute ethanol (54) in a 200 ml. ground glass stoppered Erlenmeyer flask. This flask was shielded by a cardboard container to exclude all light. A stream of dry oxygen gas was played over the surface of the ethanol for one to two minutes, then the glass stopper and cardboard cover were replaced

and the apparatus mechanically shaken in a special rotary shaker.* The oxygen atmosphere was renewed at fifteen minute intervals. Two to four hours were usually required to affect complete solution. The solution was decanted into a 250 ml. ground glass round-bottom flask. The flask was inserted in a metal box to exclude light and this was then placed in a water bath kept below 30°C. The alcohol was then removed under vacuum, using a ground glass adapter (Fig.6), and collected in a dry ice carbon tetrachloride-chloroform trap.

One to two milliliters of a pale, heavy, yellow oil were usually obtained and this was kept under a high vacuum for ten to twenty minutes after the ethanol appeared to be gone in order to remove any traces of alcohol. The oil was dissolved in 100 ml. of dry ether and this solution stored in the dark in an ice box.

Prior to use the following day, the normality of the thallous ethylate was determined by pipetting 5 ml. of the ether solution into a mixture of 20 ml. of methanol and 20 ml. of standard 0.1N hydrochloric acid. Using phenolphthalein as an indicator, the excess hydrochloric acid was titrated with standard 0.1N sodium hydroxide. Pure anhydrous ether was then used to dilute the thallous ethylate solution to 0.1N. While this solution could be kept for several weeks under the conditions specified, it was found advisable to use it within a day or so after preparation to avoid any decomposition of the thallous ethylate and to obtain best results. This quantity of thallous ethylate was sufficient

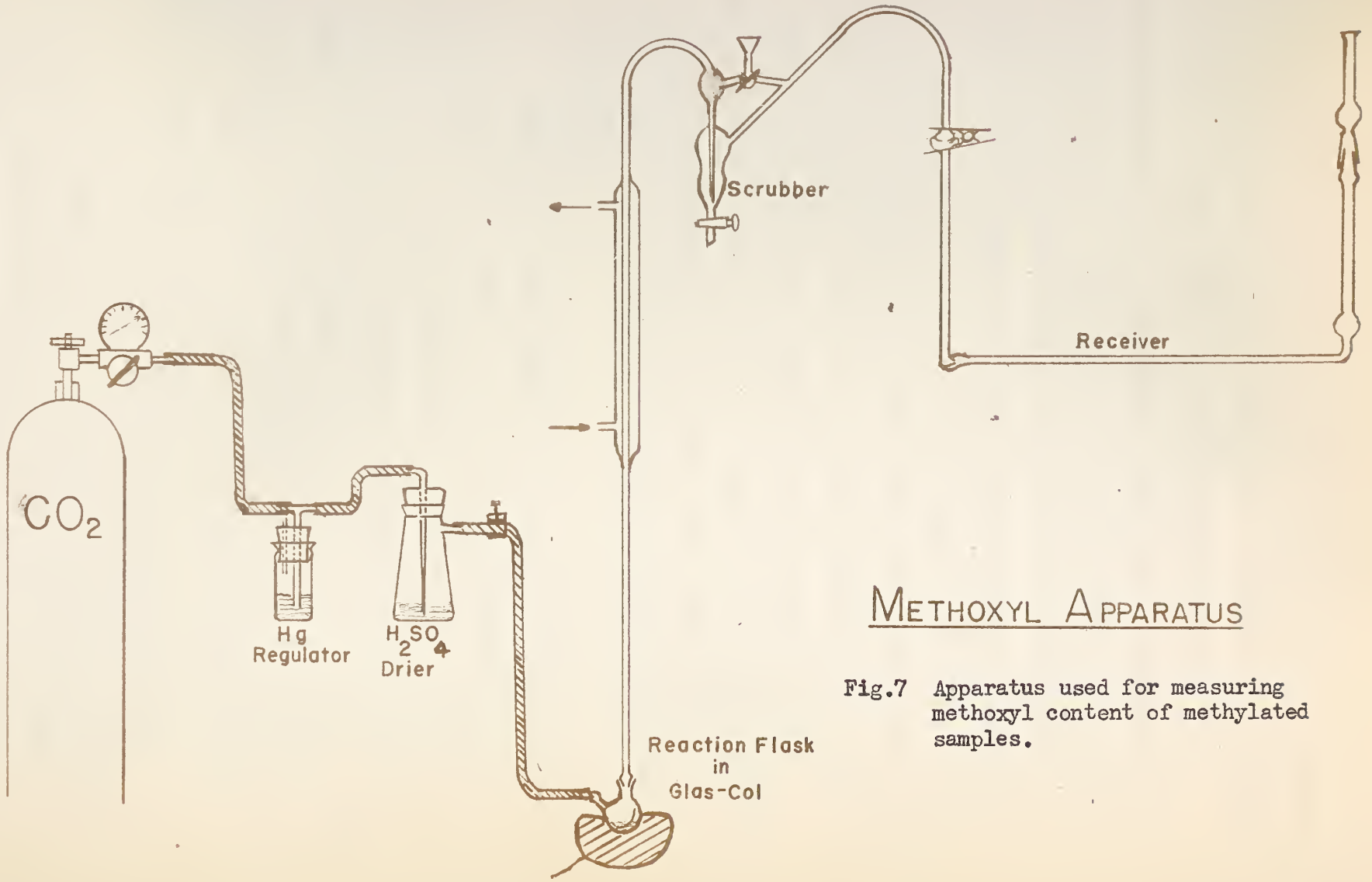
* J.W. Robinson, Tofield, Alberta, kindly made this on order.

for two large units, or twenty-four cups.

II. Determination of Accessibility by Methoxyl Estimation

The method of Hoffman and Wolfrom (41), which is a modification of the volumetric procedure of Viebock and Schwappach (42), was used for the determination of the methoxyl content of the methylated cellulose.

A set of three all-glass units were assembled as shown in Fig.7. All ground glass joints were lubricated with Lubriseal stopcock grease. (Silicone grease was tested and found in even minute amounts to give abnormally high methoxyl values.) The whole apparatus was flushed initially with a slow stream of carbon dioxide for approximately ten minutes. To each reaction flask, 8 ml. of methoxyl grade hydriodic acid and a two inch piece of nichrome wire (to prevent bumping) were added while the carbon dioxide was temporarily cut off. The scrubbers were charged by the upper stopcock with freshly mixed scrubber solution of aqueous cadmium sulfate and aqueous sodium thiosulfate. The carbon dioxide was then turned on to give a slow steady stream for about ten minutes before the variacs were adjusted to give a reflux temperature of approximately 165°C (checked by calibration). The hydriodic acid was refluxed for two hours in the stream of carbon dioxide to remove all traces of impurities (55). The variacs were then shut off and the reaction flasks allowed to come to room temperature, whereupon the flow of carbon dioxide was shut off. The scrubber solution was replaced and the receiver was then rinsed twice with glacial acetic acid and charged with 10 ml. of the receiver solution. After the receiver was connected (by the special ball and socket, flexible, ground glass joint, added as an improvement over the old rigid taper



METHOXYL APPARATUS

Fig.7 Apparatus used for measuring methoxyl content of methylated samples.

joints), the cellulose sample was quickly transferred from the thallation cup into the reaction flask with a small pair of forceps. The condenser was immediately connected and the reaction flask gently swirled to mix the hydriodic acid with the sample. The carbon dioxide flow was then adjusted to give a steady stream of bubbles through the receiver unit, which was adjusted at such an angle that each bubble remained in contact with the solution from five to seven seconds. The variac was set to give a digestion temperature of approximately 60°C. and the reaction flasks frequently swirled until the cellulose went into solution, whereupon the voltage was increased to permit vigorous reflux. Five hours later the apparatus was allowed to cool and with the carbon dioxide shut off, a second receiver was connected after fresh scrubber solution had replaced that previously used. The carbon dioxide was once more turned on and the variacs adjusted to reflux temperature for three more hours.

While the second receiver was on, the contents of the first were washed into a 250 ml. Erlenmeyer flask containing 25 ml. of water and 5 ml. of 25% sodium acetate. Ten drops of 90% formic acid were then added, the flask being swirled periodically until all the bromine color was discharged and the stopper, when loosened, showed no gas pressure to indicate the reaction incomplete. The flask was allowed to stand until the contents of the second receiver had been similarly treated in a second flask.

To each flask was added 5 ml. of 10% sulfuric acid, followed by approximately 0.5 g. (an excess) of potassium iodide and the liberated iodine was titrated with 0.02N sodium thiosulfate, using fresh starch indicator. The titrations were made using a 10 ml.

precision automatic microburet. The volume of sodium thiosulfate required for a blank determination was then subtracted from each determination. The usual practice was to add the totals for first and second receivers, then subtract twice the value of the blank. In most cases the value for the second receiver closely approximated that of the value for the blank.

Calculations were based on the following equations:

$$\text{Wt. of Methoxyls} = \frac{\text{Vol. } Na_2S_2O_3 \text{ (ml.)}}{1000} \times \text{Normality } Na_2S_2O_3 \times \frac{31}{6}$$

$$\% \text{ Accessibility} = \frac{\text{Wt. of methoxyl}}{\text{Wt. of sample}} \times 100 \times \frac{100}{57.4}$$

Trimethyl cellulose has a methoxyl content of (3 x 31 x 100)/162, or 57.4% on this basis. For convenience in calculating these two equations were condensed to give a conversion factor including the normality and the constants, to the form:

$$\% \text{ Accessibility} = (\text{Conversion factor}) \times \frac{\text{Vol. } Na_2S_2O_3}{\text{Wt. of sample}}$$

Reagents for Methoxyl Estimation

The scrubber solution consisted of a mixture of equal volumes of 5% aqueous cadmium sulfate with 5% aqueous sodium thiosulfate. It was found advisable to store the 5% solutions in separate bottles and mix them freshly before using.

Carbon dioxide was most satisfactorily supplied by a tank obtained rent-free from Liquid Canadian Carbonic Corp. The carbon dioxide was dried by bubbling it through concentrated sulfuric acid, the gas flow being controlled both by a very efficient gauge on the

tank, and also a pinchclamp on the rubber tubing. (Fig.7)

The receiver solution was prepared by dissolving 105 g. of potassium acetate in 1050 ml. of glacial acetic acid and adding 21 ml. of bromine. The solution was then exposed to daylight (to stabilize the solution) in a clear glass bottle for at least a week before use.

The sodium thiosulfate contained 0.20% of sodium carbonate as a preservative. Frequent standardizations were carried out using aliquotes of a standard potassium iodate solution according to standard techniques (56).

III. Nitrations of Cotton Linters

(a) Using Sulfuric Acid - Nitric Acid Mixtures

The nitration procedure was identical to that employed by Brown and Purves (2). Technical nitration mixtures were made up, according to the tables assembled by J. Barsha (47), to yield a nitrated cellulose of approximately ten to eleven per cent nitrogen. Sample nitrations were made and the acid mixture also analysed to check the nitration strength of the acid (57).

All nitrations were carried out under carefully controlled conditions to ensure reproducible results. One hundred grams of the technical nitration solution were put in a dried, glass-stoppered, 250 ml. Erlenmeyer flask. The flask and contents were brought to 15°C. in a constant temperature bath, and one gram of dried cellulose was quickly weighed (to the second decimal place), roughly shredded with forceps, and immersed in the nitration fluid. The nitration proceeded for exactly thirty minutes at 15°C. with frequent shaking of the flask to ensure thorough mixing. The thirty minute reaction time was chosen

to conform to that commonly used in industry, while 15°C. was chosen as a temperature to minimize degradation and side reactions and yet permit maximum nitration in the chosen time interval. The liquid was removed by suction through a coarse, sintered-glass funnel, and the nitrocellulose slightly squeezed to remove excess fluid. The nitrated product was then thrown in very small pieces into 250 ml. of a rapidly stirred 1:1 mixture (by weight) of ethanol and water, previously cooled to -15°C. The liquid was again removed by suction through a clean, sintered-glass funnel into a second suction flask free of alcohol. The solid was pressed lightly to remove excess fluid. Two more such washings in 100 ml. portions of cold aqueous ethanol were followed by four similar immersions in more of the same ethanol-water mixture at room temperature. Completeness of removal of free acid was tested by litmus. The washed cellulose nitrate was subsequently boiled for five minute periods in three successive 100 ml. portions of 1:1 ethanol-water solutions previously heated to the boil. Such treatment is reported to remove any bound sulfuric acid and to yield a thoroughly stable nitrocellulose (58,59,60). The hot liquid was removed as before and the cellulose nitrate was dried in a dessicator over phosphoric anhydride under vacuum, and when dry, was stored over phosphoric anhydride until ready for analysis.

The technical nitrocelluloses thus obtained were colorless and fibrous, but more brittle in texture than the original material, suggesting the occurrence of degradation during nitration.

(b) Extended Nitration Period

Nitration of samples was identical with the procedure described above with the one exception of time. Instead of the thirty

minute nitration period used in (a), the samples remained in contact with the nitration mixture for ninety minutes. The same nitration mixture was used for this nitration as for the shorter thirty minute periods.

IV. Analysis for Nitrogen Content

(a) Semi-micro Keldahl

Samples of dry nitrocellulose were analysed as outlined in Rosenthal's thesis (61). Approximately 0.1 g. of dry sample was quickly and accurately weighed out on a cigarette paper of known weight from which the gummed edge had been removed. The paper with the sample was inserted into a clean dry 300 ml. Kjeldahl flask, and 0.3 g. salicylic acid along with 10 ml. of concentrated sulfuric acid was added. After a digestion period of one hour at room temperature the sample was found to be completely dissolved. Then 0.8 g. (1.25 g. of hydrated) anhydrous sodium thiosulfate was added and the flask warmed gently until effervescence ceased. After 2.0 g. of powdered potassium sulfate and a tiny pinch of selenium catalyst (49) had been added, the flask was gently heated under a hood until the evolution of gas became less pronounced, then more strongly until the liquid was clear and colorless. An extra half hour of heat ensured complete digestion but care was taken to prevent loss of the sulfuric acid. More sulfuric acid was added if necessary to maintain its initial concentration. The flask was then cooled.

After a dilution with 100 ml. of distilled water, 50 ml. of 40% sodium hydroxide was carefully added down the side of the flask. A few small bits of mossy zinc were added to prevent bumping and when the flask had been connected to a still-head and condenser, about

75 - 100 ml. of liquid were distilled into 30 ml. of 4% aqueous boric acid solution containing 10 drops of special mixed indicator of methyl red and brom-cresol green (50). This was immediately titrated with 0.02N hydrochloric acid to the disappearance of the greenish color and the first faint appearance of the red.

It was necessary to run a blank and apply a correction to the final readings. The per cent nitrogen was obtained by the equation

$$\text{Per cent N} = \frac{\text{Vol. HCl (ml.)}}{1000} \times \frac{\text{Normality HCl}}{\text{Sample weight}} \times 14.01 \times 100$$

Reagents

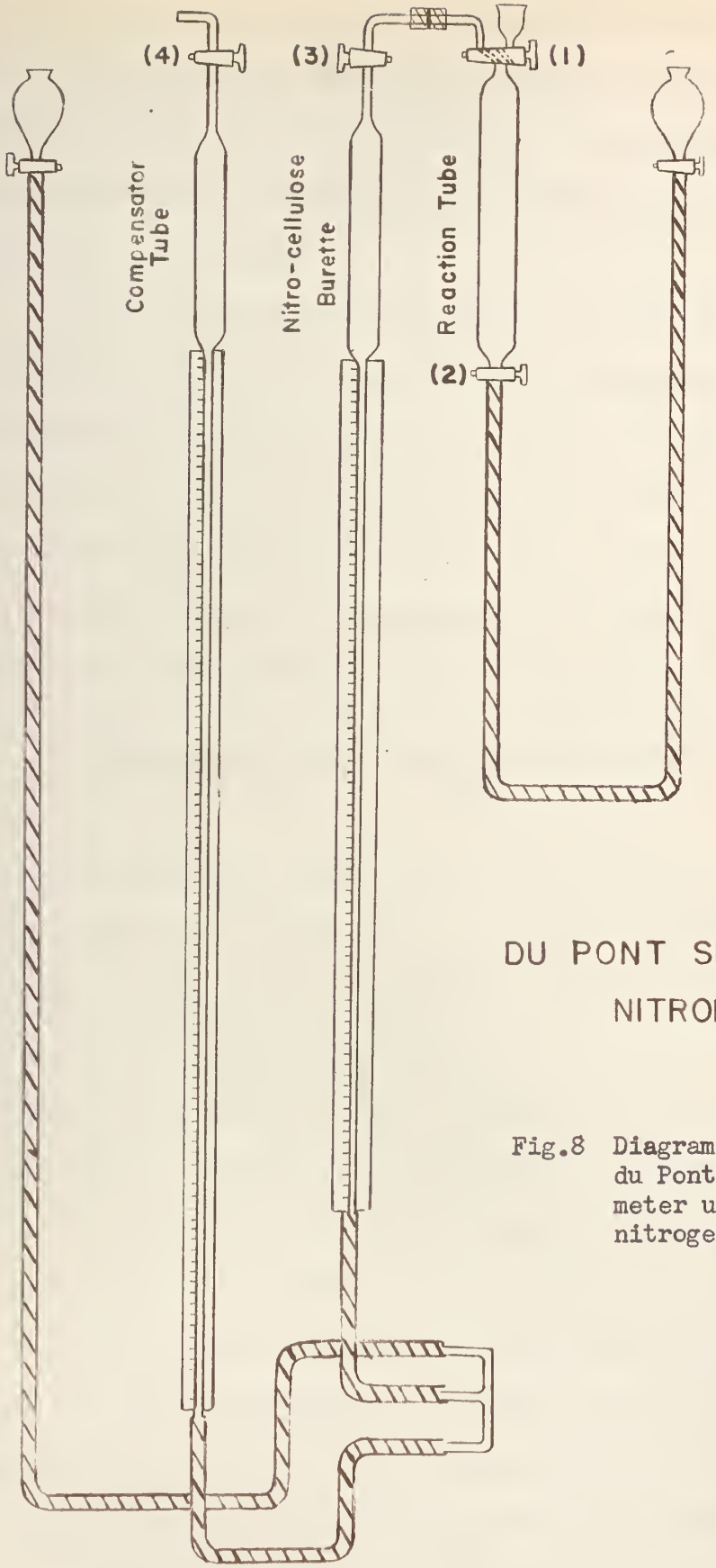
The 4% boric acid solution was prepared by adding to boiled distilled water the correct weight of solid boric acid. The solution was again boiled to expel the last traces of carbon dioxide. The volume decrease due to evaporation was made up by adding more boiled distilled water. It was then stored in a pyrex, glass-stoppered bottle.

The mixed indicator consisted of a solution of 2 ml. of a one per cent solution in ethanol of methyl red in 10 ml. of a one per cent solution in ethanol of brom-cresol green (50).

(b) Du Pont Semi-micro Nitrometer

Rapid, accurate analyses were carried out on cellulose nitrate samples using a du Pont Nitrometer built to the specifications of Elving and McElroy (52).

A hand shaken model (Fig.8) was calibrated by mercury displacement to convert scale readings in centimeters to volume in milliliters. This data was plotted and all readings from the scales were converted to volumes by use of the graph.



DU PONT SEMI-MICRO NITROMETER

Fig.8 Diagram of the hand-shaken du Pont semi-micro nitrometer used in nitrate nitrogen determinations.

Initially the compensating tube, nitrocellulose burette, reaction tube, and all connections and capillaries were completely filled with purified mercury (62), particular care being taken to remove air bubbles. With the system thus filled, stopcocks 1, 3, and 4, were closed and the levelling bulbs adjusted approximately to the height of these stopcocks.

The apparatus was standardized with potassium nitrate (52). Approximately 105 mg. of potassium nitrate, previously purified by twice recrystallizing from water, then washed with alcohol, and oven-dried at 150°C., was accurately weighed to the fifth decimal place. Since at standard temperature and pressure, 100 mg. of pure potassium nitrate give 22.15 ml. of nitric oxide, to calculate the theoretical volume at the same conditions, the following equation was used.

$$\text{Theoretical volume} = \frac{\text{Wt. } KNO_3 \text{ (mg.)}}{100} \times 22.15$$

The weighed sample was placed in the cup on top of the reaction tube and the tared glass weighing cup was reweighed. The potassium nitrate was washed into the reaction tube with six one-milliliter portions of concentrated, nitrogen-free, sulfuric acid, using a 1 ml. pipet with rubber bulb attached. It is very important that no air be admitted with the sample. Stopcock 1 was closed and the reaction tube disconnected from the nitrocellulose burette and shaken until gas pressure forced the mercury down to approximately an inch from the bottom stopcock 2. This stopcock, 2, was then closed and shaking continued for three periods of about two minutes each, allowing a short interval between shakings. Care was taken to keep the mercury in the capillary above stopcock 1 by keeping a finger over the end while shaking. The reaction

tube was then connected to the nitrocellulose burette by the rubber coupling, in such a manner that the ground-glass faces fitted together.

The capillary above stopcock 4 was filled with mercury, then 4 was opened and sulfuric acid-dried air was drawn in to give a volume slightly greater than that calculated for the sample used. The levelling bulb was then gently raised to give the correct volume by expulsion of excess air and stopcock 4 was closed. The correct volume reading is made when the mercury in the levelling bulb is at the same height as the mercury in the compensator tube.

The compensator bulb was then raised well above the level of the top of the apparatus, and stopcocks 3 and 1 were opened in that order so that mercury flowed from the nitrocellulose burette and rinsed the sulfuric acid from the capillary below stopcock 1. The levelling bulb was now lowered and the gas drawn over until the liquid in the reaction tube came just to the top edge of stopcock 1. Stopcocks 1 and 3 were then closed. The levelling bulb and compensator tube were then adjusted so that with the mercury in the nitrocellulose burette, and compensating tube at the same level, the reading on the nitro-cellulose burette corresponded to the calculated theoretical volume. The scale reading on the compensator tube was then recorded and used as the standardization mark for subsequent determinations, since it now would convert all readings to standard conditions.

To make an analysis, it was necessary to know the approximate nitrogen content of the sample. Basing calculations on the fact that 100 mg. of 14% nitrogen would give a volume of approximately 23 ml. which could be read on the scale nicely, a sample of approximately 140 mg. was found to be best. The sample was accurately weighed out

in a tared weighing cup and transferred to the cup on top of the reaction tube as in the standardization. The tared cup was weighed again and sample weight calculated from these values. It was found necessary to correct these weights for the amount of moisture absorbed by the nitrocellulose in coming from the dry state over phosphoric anhydride to equilibrium with room conditions.

The sample was introduced into the reaction tube by carefully flushing with six one-milliliter portions of concentrated sulfuric acid and judiciously pushing the sample particles through the bore of the stopcock with a smooth-ended fine tantalum wire. It was essential that all the sample was well rinsed into the reaction tube and at the same time no air admitted. The reaction tube was shaken as in the standardization, but the compensator tube was left unchanged. The gas was transferred to the burette as before. To make a reading, the columns of mercury in the nitrocellulose burette and compensator tube were adjusted so that they were level when the compensator tube read at the standardization mark. The reading on the nitrocellulose burette was then taken. This was the volume of nitric oxide at standard conditions.

The per cent nitrogen was calculated from the equation,

$$\text{Per cent nitrogen} = \frac{\text{Vol. in ml. NO} \times 62.56}{\text{Sample wt. in mg.}}$$

The apparatus was emptied by forcing the gas back into the reaction tube and leaving the capillary between stopcocks 1 and 3 full of mercury. The gas and acid were then sucked by a water pump from the filling cup into a trap. The cup and reaction tube were rinsed with a small amount of sulfuric acid and the unit was ready for the next determination. Total time required was about twenty

minutes for a complete determination.

(c) Moisture Equilibrium Correction

Nitrated samples were stored in the bone-dry state over phosphoric anhydride under vacuum. Since the dried nitrates were extremely hygroscopic, erroneous values for the sample weights occurred due to moisture adsorption during manipulation of samples. To eliminate this error, samples were placed in tared weighing bottles and thoroughly dried over phosphoric anhydride, then rapidly capped and weighed in their dry state. The weighing bottles were then uncapped and exposed to room conditions for a day and reweighed. From the increase in weight was calculated the percentage of moisture absorbed and the true weight was obtained by the following relation,

$$\frac{100 - \%\ \text{moisture absorbed}}{100} \times \text{Sample weight} = \text{True Sample Weight.}$$

Nitrogen contents were then calculated on the basis of this true sample weight.

V. Hydrogen - Deuterium Exchange

An empirical value was calculated as a measure of the percentage of hydroxyls accessible to heavy water by determining the degree of exchange of deuteriums for hydrogens in a cellulose sample. The apparatus and technique of Frilette, Hanle, and Mark (4,63), were used with but a few modifications. The course of the reaction was followed by measurement of changes in the specific gravity of samples of diluted deuterium oxide using the falling drop method of measuring specific gravity. Clear solutions of purified ∝-methyl naphthalene and phenanthrene, of definite concentration and specific gravity,

measured at 25° ± .002 and the reference liquids, kept at this temperature, were protected from light to prevent decomposition of the solution.

The optimum densities of the reference solutions put a limiting density on the maximum concentration of heavy water at approximately 40%. For the present work it was necessary to dilute 98% deuterium oxide to 40%.

Since reproducible results are obtained only by the careful observation of certain points of technique, a typical determination is described in detail.

Approximately one gram of cellulose was put into the weighed reaction cell (Fig.9a), fitted with a glass stopper (not shown), and the unit weighed again to determine accurately the amount of cellulose. Five milliliters of heavy water was added by pipet, at zero time, and the whole apparatus again weighed to ascertain the amount of heavy water. The mixer assembly then replaced the glass stopper and when the cell was placed in the constant temperature bath at 25° ± .002, the sample was thoroughly agitated with the mixer rod at frequent intervals.

Samples of heavy water were removed from the reaction cell using a calibrated 0.1 ml. pipet (Fig.9b). The reaction cell was tilted and the stirring rod pressed into the cellulose in such a way that a drop of water would run into the narrow side arm to form an air lock. The dry capillary pipet (Fig.9b), fitted with the bulb of a medicine dropper (not illustrated), was inserted through the side arm of the reaction cell and a sample of liquid drawn up from the cellulosic mass. The capillary was then removed and wiped dry with hard filter paper. Manipulation of the water sample was facilitated by a small hole at the top of the rubber bulb which was closed and opened at will by the index finger. The pipet was inserted into the

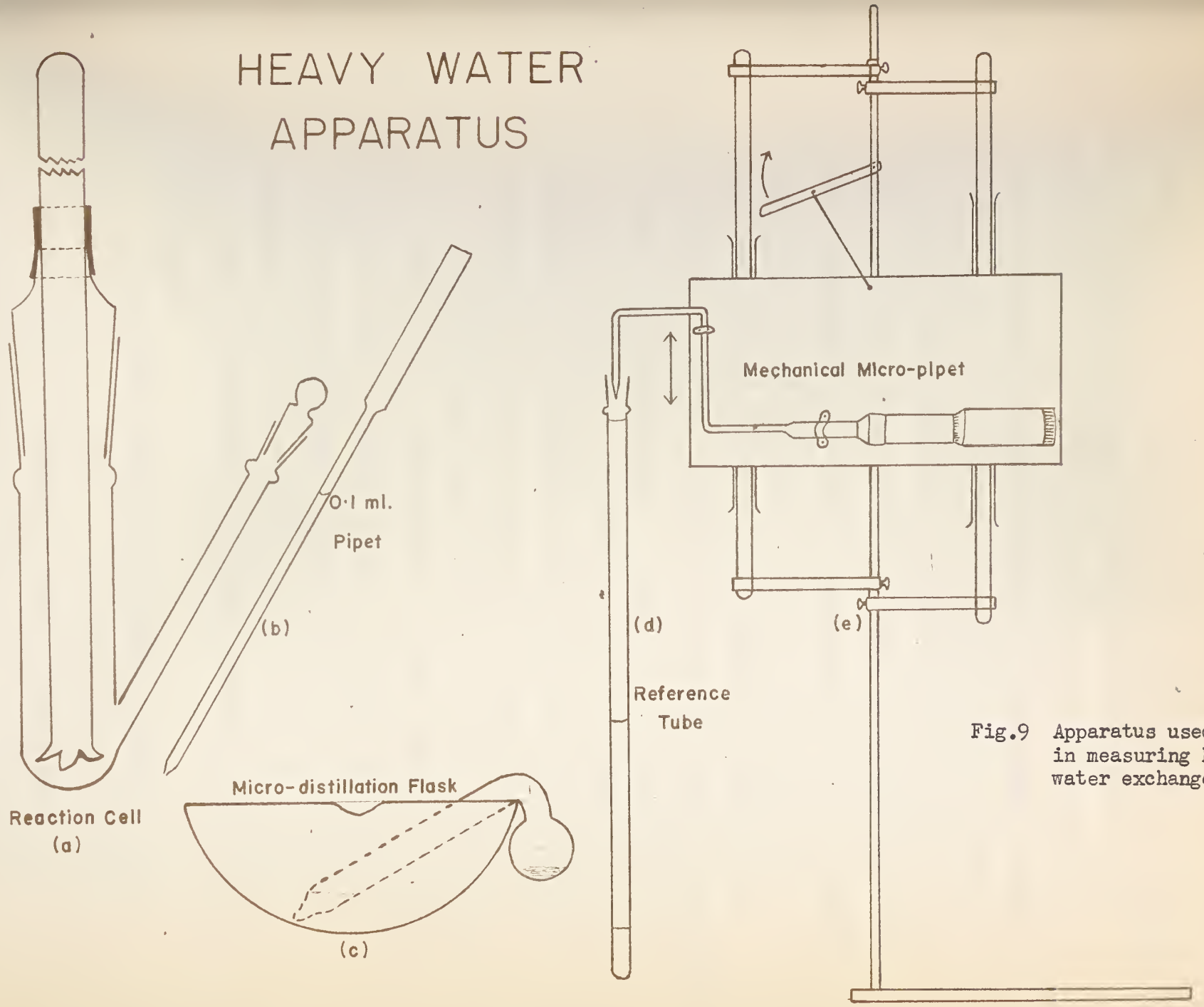


Fig.9 Apparatus used in measuring heavy water exchange.

narrow opening of the carefully dried micro-distillation flask (Fig.9c) until it touched the back wall of the flask and the liquid was then forced into the bulb. The tip of the pipet was rotated against the portion of the horizontal tube adjoining the bulb in order to remove any large excess of water, after which it was carefully withdrawn so as to avoid contamination of the receiver portion of the flask. The flask containing the sample was then evacuated to approximately 20 mm. and the neck quickly sealed off with a hand torch. Prior to analysis, these flasks were kept in racks and placed in such a way that the sample remained in the bulb. By simply hanging the flask with the receiver in ice water in a shallow evaporating dish (Fig.9c), distillation to dryness was attained in about one-half hour. It is important that the retorts be stored in a dessicator before use to ensure a dry inner surface, and that the evacuation step be carried out very rapidly so that the flask is sealed off before any of the water is distilled.

When distillation was complete, the flask was removed from the ice bath, the tube, maintained in a vertical position, was wiped dry and cut so that the receiver became a convenient micro-beaker containing the purified water. To give a dry cut, the pyrex micro-distillation flasks were file-marked and the molten end of a soft glass rod was placed against the cut which caused it to crack around at this point.

The specific gravity of the liquid was determined by the falling drop method. Since it was imperative that the drop size remain constant for all readings, a tight fitting hypodermic all-glass syringe was equipped with a micrometer attachment similar to the model used by Dr. R.N. Jones of the National Research Council of

Canada. This was mounted on a piece of 3/8" plywood, which, in turn was clamped on the inexpensive elevating mechanism shown in Fig.9e. (This apparatus operated as an economical drill press.)

The pipet was carefully filled with purified mercury (62), care being taken to exclude air bubbles. During operation, the micrometer was turned until a drop of mercury formed on the tip of the pipet, the tip was then inserted below the surface of the sample and a few drops of mercury were forced out. The sample was then drawn up and a minute portion of the mercury previously forced out was drawn back into the tip to seal in the sample of heavy water during manipulations.

Ten scale divisions on the drum of the micrometer employed, gave a drop of suitable and reproducible size. The drop size was calculated from the weight of the mercury extruded at a definite temperature (25°C.) by turning the micrometer through exactly two hundred scale divisions on the drum (two complete revolutions). The volume displaced was calculated from tables (77). By this method the average drop radius was found to be 1.13 mm., and the volume, 6.06 cu. mm.

Reference liquids were prepared, based on the empirical relationship between specific gravity and relative weights of constituents given by Frilette and Hanle (63). The α-methyl naphthalene, obtained from Eastman Kodak, was thrice distilled, the clear middle fraction being taken each time. The final product was that fraction distilling at 90 - 91°C. under a pressure of 0.5 - 1.0 mm. The technical grade phenanthrene was recrystallized three times from 98% ethanol.

Using the equation,

$$S_o = 1.011 + 0.001C + 0.0004(30 - t°)$$

where, S_o = specific gravity of reference solution at t°/t°

C = grams of phenanthrene added per 100 g. of ∝-methyl naphthalene

t° = temperature of the thermostat in °C.,

five reference solutions were made up which had specific gravities approximately 1.01, 1.025, 1.030, 1.035, 1.040. These were placed in reference tubes (Fig.9d) equipped with ground glass stoppers. The tube dimensions were: height, 55 cm.; inside diameter 1.0 cm.; marked with rings at 8 cm. and 23 cm. from the bottom (64).

The actual specific gravities at 25°C. were then determined using the previously mentioned Leach specific gravity bottles.

Difficulty was experienced with the reference liquids darkening when exposed to the fluorescent lighting of the laboratory. After several days, dark particles appeared on the surface or interface between the heavy water and reference solution. This necessitated filtering, cleaning the tube and repeating the calibration.

The tubes were calibrated with a sample of heavy water which had been freshly distilled and whose specific gravity had been determined at 25°C using the 1 ml. pycnometer. Stokes Law (65) states that,

$$6\pi\eta\frac{rdx}{dt} = \frac{4}{3}\pi r^3(dp - dm)g$$

or, $$\eta = 14.5185\ r^2dt(dp - dm)$$

where, η = coefficient of viscosity

r = radius of drop in cm.

g = 980 cm./sec./sec.

dx = distance measured = 15 cm.

dt = time to fall dx cm. (in sec.)

dp = density of heavy water drop

dm = density of reference solution

Substituting these values, for any given determination using the same reference solution, in the equation,

$$dp = dm - \frac{\text{constant}}{dt}$$

it is possible to determine the density of the falling drop. At least ten drops were averaged in order to determine the falling time.

To correct for residual moisture in the cellulose, a duplicate sample of cellulose was taken and analysed for moisture content by drying in an air-oven under vacuum at 110°C. according to standard practice. To the experimentally determined quantity of residual moisture was added an arbitrary correction of 0.5%, since it is known that cellulose dried under the described conditions tends to retain this amount of water (66).

In this method of calculating the degree of exchange, two assumptions were made:

(a) The moisture present in the cellulose sample very rapidly dilutes the heavy water.

(b) All three cellulose hydroxyls are indistinguishable in so far as the rate of exchange is concerned.

The exchange equilibrium may be written as:

$$2\ R(OH)_3 + 3\ D_2O \rightleftarrows 2\ R(OD)_3 + 3\ H_2O$$

For complete reaction, the number of moles of deuterium oxide consumed for an infinite excess of 100% deuterium oxide is given by,

$$\frac{(1 - 0.01m)x}{108.1} \qquad (i)$$

where, x = grams of cellulose used

m = percentage of moisture content of x (wet basis)

Z = moles of water ($D_2O + H_2O$) added to cellulose.

E_o = initial mole fraction of D_2O in heavy water.

E_t = mole fraction of D_2O in heavy water at time t.

F = extent of reaction, i.e. number of cellulose hydroxyls which have exchanged D for H, divided by the number of such groups which would exchange if all of them were in equilibrium with the water.

W = original weight of heavy water added to the cellulose.

For a finite amount of dilute heavy water, the number of moles consumed at time t is given by,

$$E_tF\,\frac{(1 - 0.01m)x}{108.1} \qquad \text{(ii)}$$

By definition, using assumption (a)

$$E_t = \frac{E_oZ - E_tF\left[\frac{(1 - 0.01m)x}{108.1}\right]}{Z + \frac{0.01mx}{18.02}} \qquad \text{(iii)}$$

since,

$$E_t = \frac{\text{moles } D_2O \text{ initially present - moles } D_2O \text{ used}}{\text{Total moles } (D_2O + H_2O)} \qquad \text{(iv)}$$

Expressing in terms of weight of heavy water,

$$W = 20.0E_oZ + 18.01(1 - E_o)Z \qquad \text{(v)}$$

This equation can be used to eliminate the Z terms in equation (iii).

To eliminate the mole fractions E_o and E_t, let the corresponding specific gravities be S_o and S_t. The relationship between E and the corresponding S may be written

$$E = \frac{(S - 1.00000)}{0.1080} \qquad \text{(vi)}$$

Consideration of equations (iv,v,vi) with appropriate transpositions leads to the final relationship for F in terms of the weights of materials used and the observed specific gravities.

$$F = A\left[\frac{S_o - S_t}{S_t - 1}\right] - B \qquad \text{(vii)}$$

where A and B are constants in any given reaction, and their equivalents are:-

$$A = \frac{108.1\ W}{(18.02 + 2E_o)\ (1 - 0.01m)x} \qquad \text{(viii)}$$

$$B = \frac{1.081m}{18.02\ (1 - 0.01m)}$$

According to the literature (63) it is possible to determine F within 2×10^{-2}. In other words, about 1 or 2 % in terms of percent of the hydroxyls exchanged.

In accordance with the theory of precision of the determination, reference solutions were chosen for each determination which most closely approximated the density of the heavy water being tested (63).

VII. Moisture Absorption at a Constant Relative Humidity

In a large clean dessicator, suitable for storing the samples, was prepared a mixture of 250 ml. water and 130 ml. of concentrated sulfuric acid, which provides an atmosphere of fifty percent humidity (67). The dessicator was allowed to stand for eight days, then a sample of the mixture was withdrawn and titrated with standard alkali. The acid was calculated to be 45% in strength which according to tables (67) gives a 45% relative humidity.

Dry samples in tared weighing bottles were weighed, then placed in a low flat dish and the tops set on an angle for ease in

subsequent handling. The dish was placed on a porcelain rack in the dessicator and the samples were allowed to absorb water from the sulfuric acid-controlled relative humidity. Before measuring weight increase, the tops of the weighing bottles were quickly tipped back on before the container was lifted out of the dessicator. Weights were recorded and a sample of acid withdrawn and titrated to determine the relative humidity. Then samples were replaced in the same dessicator with tops ajar for further absorption. The acid concentration was found to be practically the same as initially, so no correction was required for change in relative humidity.

DISCUSSION AND RESULTS

The cellulose for our experimental work was prepared by removing residual fats and waxes from cotton linters, over a period of fifty hours, with a 1:2 solution of ethanol-benzene in a Soxhlet apparatus. Since the adhering solvent was removed from the linters by evaporation, the ethanol should be eliminated as an azeotropic mixture (70) before the last of the benzene. It follows therefore, that because the polar solvent ethanol has swelling properties (71), this would constitute drying by solvent exchange (25) and hence tend to leave the linters in a partially swollen state.

Part of this solvent-free linters was immediately wetted to prepare samples for Series I (Table I), another portion was stored over concentrated sulfuric acid, while the remainder of the dewaxed material was stored in a large glass jar with no drying agent. Preparation of samples for Series II, as confirmation of results for Series I, was begun a year later, at which time a small sample (II-0) of the dewaxed linters, kept for a year in a jar without a desiccant, was stored over phosphoric anhydride under vacuum while about seventy grams of this same linters was given its first wetting. This difference in storage time appears to be important in comparison of accessibility values for the two series, particularly for the control samples of original unwetted linters (I-0, II-0) and those samples having received only one wetting and drying treatment (I-1, II-1). Each series was given twenty-five wetting and drying cycles carried out under room temperature conditions and eight samples from

each set, chosen after the appropriate number of cycles, were stored over a desiccant. Series I was kept over concentrated sulfuric acid, then later over phosphoric anhydride, while Series II was immediately placed over phosphoric anhydride. Accidentally the temperature rose to 70°C. during wetting number nineteen in Series I. This is the only case in which the wetting temperature deviated from room temperature and its effect on the linter sample taken after this wetting was similar to that found in the high temperature wetting Series HT.

Approximately two months after the first sample of Series I, (I-0), had been placed over sulfuric acid, a third series of linter samples designated HT was begun using the same original dewaxed linters, which had remained stored with no drying agent. A small portion (HT-0) was put over sulfuric acid without any previous wettings, while the remainder was six times alternately wetted with water at approximately 80°C. and dried over phosphoric anhydride (Table III). The samples HT were stored in the same desiccator which held Series I.

Since Schur and Hoos have clearly shown that the mode of mechanical manipulation of pulps does affect their properties to a small but significant degree (72), a few linter samples were prepared differing in their mechanical preparation in order to estimate the degree to which these treatments might influence our results. The details of the treatment are shown in Table IV. Samples S-IV and S-V were wetted, S-IV with vigorous stirring and S-V with no agitation, then excess water was removed by filtration, using firm pressure on

S-V only. For comparison, S-II was water-wetted with no stirring and no pressing to remove excess water. I-10A and S-III were dried by solvent exchange, S-I was the original linters, and C-I, a sodium carbonate-swollen linters, completed the special treatments.

In addition, several samples from Series I (I-0, I-1, I-25), were exposed to the atmosphere in the laboratory office for six months to determine whether such treatment could produce a levelling effect on the properties of linters known to have different accessibilities prior to exposure.

TABLE IV

SPECIAL TREATMENTS OF SOME SAMPLES OF DEWAXED COTTON LINTERS[a]

Sample	Treatment
I-10A	Sample from 10 cycles of Series I. Dried by solvent exchange.
S-I	Sample of original unwetted, dewaxed cotton linters for control.
S-II	Original dewaxed cotton linters immersed for 3 hours in distilled water, dried under vacuum over phosphoric anhydride to compare with S-III.
S-III	Original dewaxed cotton linters immersed for 3 hours in distilled water, solvent exchange dried. Stored together with S-II, over phosphoric anhydride under vacuum.
S-IV	Original dewaxed cotton linters mechanically stirred during 3 hour immersion at room temperature. No pressing used in removing water.
S-V	Original dewaxed cotton linters immersed for 3 hours without stirring. Excess water pressed out before drying together with S-IV over phosphoric anhydride.
C-I	Original dewaxed cotton linters swollen with 10% sodium carbonate, neutralized with acetic acid, then washed free of acid. Solvent exchange dried.

a. Samples were dried over phosphoric anhydride under vacuum, and all stored in the same desiccator containing Series I, in the dark at room temperature over phosphoric anhydride.

TABLE V

MOISTURE SORPTION OF CYCLICALLY WETTED AND DRIED COTTON LINTERS STORED IN AN ATMOSPHERE OF CONSTANT RELATIVE HUMIDITY# - SERIES I

Sample No.	Wetting-Drying Cycles	Percent Weight Increase in days				Percent Moisture Removed
		3[a]	8[a]	20[a]	44[b]	44[c] days
I-0	0	4.39	4.49	4.44	4.73	4.74
I-1	1	5.00	5.32	5.04	5.05	5.05
I-5	5	4.92	5.00	4.93	5.07	5.09
I-9	9	4.75	4.82	4.79	5.04	5.07
I-13	13	4.84	4.92	4.86	5.00	5.02
I-17	17	4.82	4.88	4.85	5.02	5.02
I-21	21	4.68	4.72	4.71	4.99	5.00
I-25	25	4.76	4.84	4.81	5.00	5.00
HT-3	3	4.97	5.05	4.99	5.04	5.04
HT-6	6	4.87	4.94	4.90	4.98	4.98

The concentration of the diluted sulfuric acid used to give a constant humidity of 45% was checked at intervals during which the linters absorbed water from the mixture. There was found to be no appreciable change in the concentration with the quantities of materials used.

a. Percent moisture absorbed based on initial weight of sample.

b. After 44 days at constant relative humidity of 45%, the samples were dried under vacuum with phosphoric anhydride for 11 days. The decrease in weight was calculated on the initial sample weights.

c. As in b., but weight decrease based on dry weight obtained.

TABLE VI

MOISTURE SORPTION OF CYCLICALLY WETTED AND DRIED COTTON LINTERS STORED IN AN ATMOSPHERE OF CONSTANT RELATIVE HUMIDITY# - SERIES I

Sample No.	Wetting-Drying Cycles	Percent Weight Increase in 10 days[a]	60 days[a]
I-0	0	4.31	4.23
I-1	1	4.71	4.67
I-5	5	4.67	4.65
I-9	9	4.66	4.68
I-13	13	4.65	4.67
I-17	17	4.64	4.67
I-21	21	4.55	4.59
I-25	25	4.61	4.55[b]

This second series was run at a constant relative humidity of 45% to check on results of Table V.

a. Percent based on initial weight of sample.

b. Low result probably due to experimental error.

Estimation of the accessibilities of these specially treated linters samples was made by reaction with (a) thallous ethylate in ether, (b) standard nitrating agent, (c) deuterium oxide. The lack of time, or insufficient amount of sample in some cases prevented analysis by all three methods.

Since linters stored in the bone-dry state are very hygroscopic, portions of each sample from Series I were stored

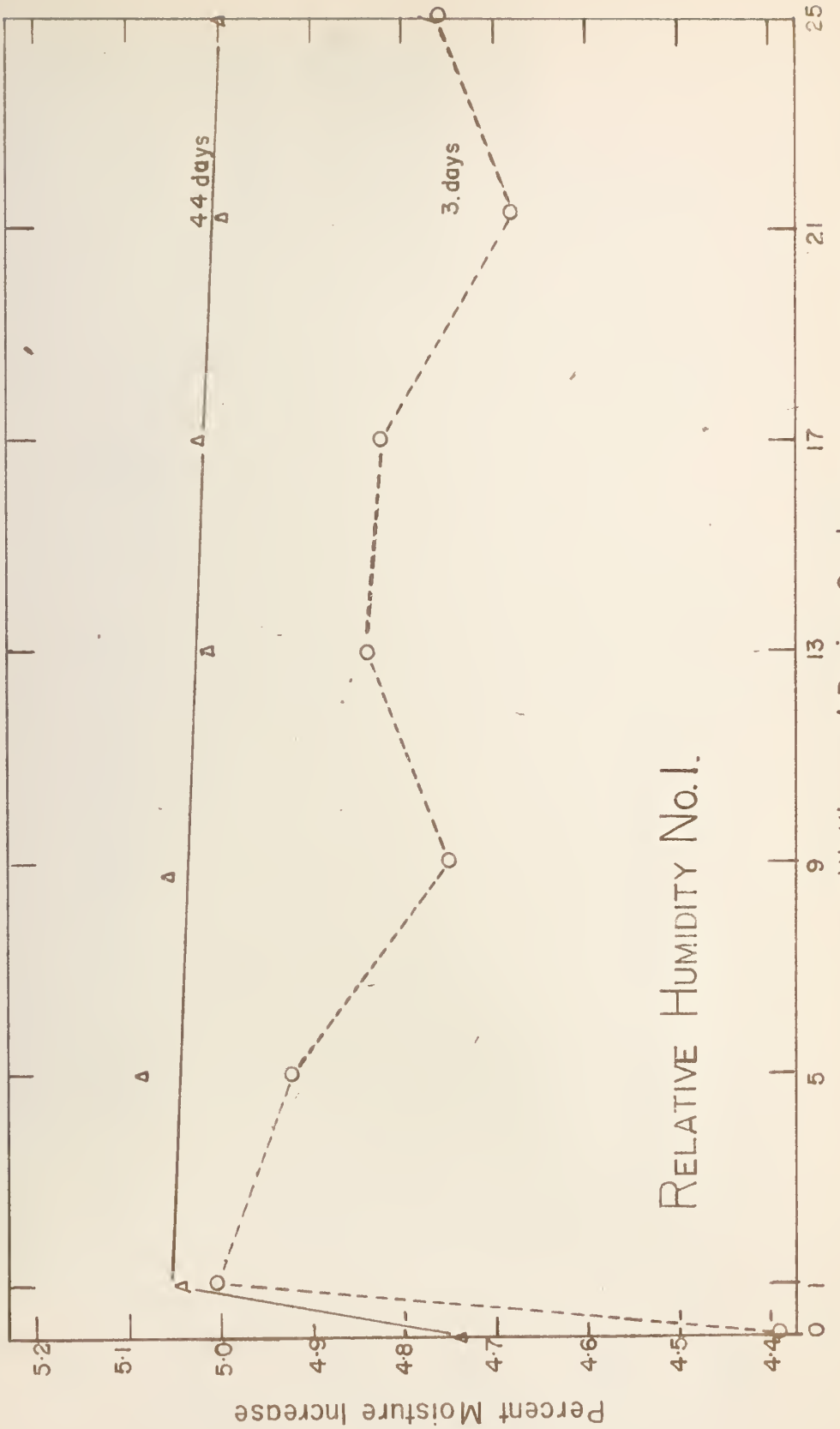


Fig.10 Water Sorption of Dried Linters (Series I). Water absorbed from an atmosphere of relative humidity 45%.

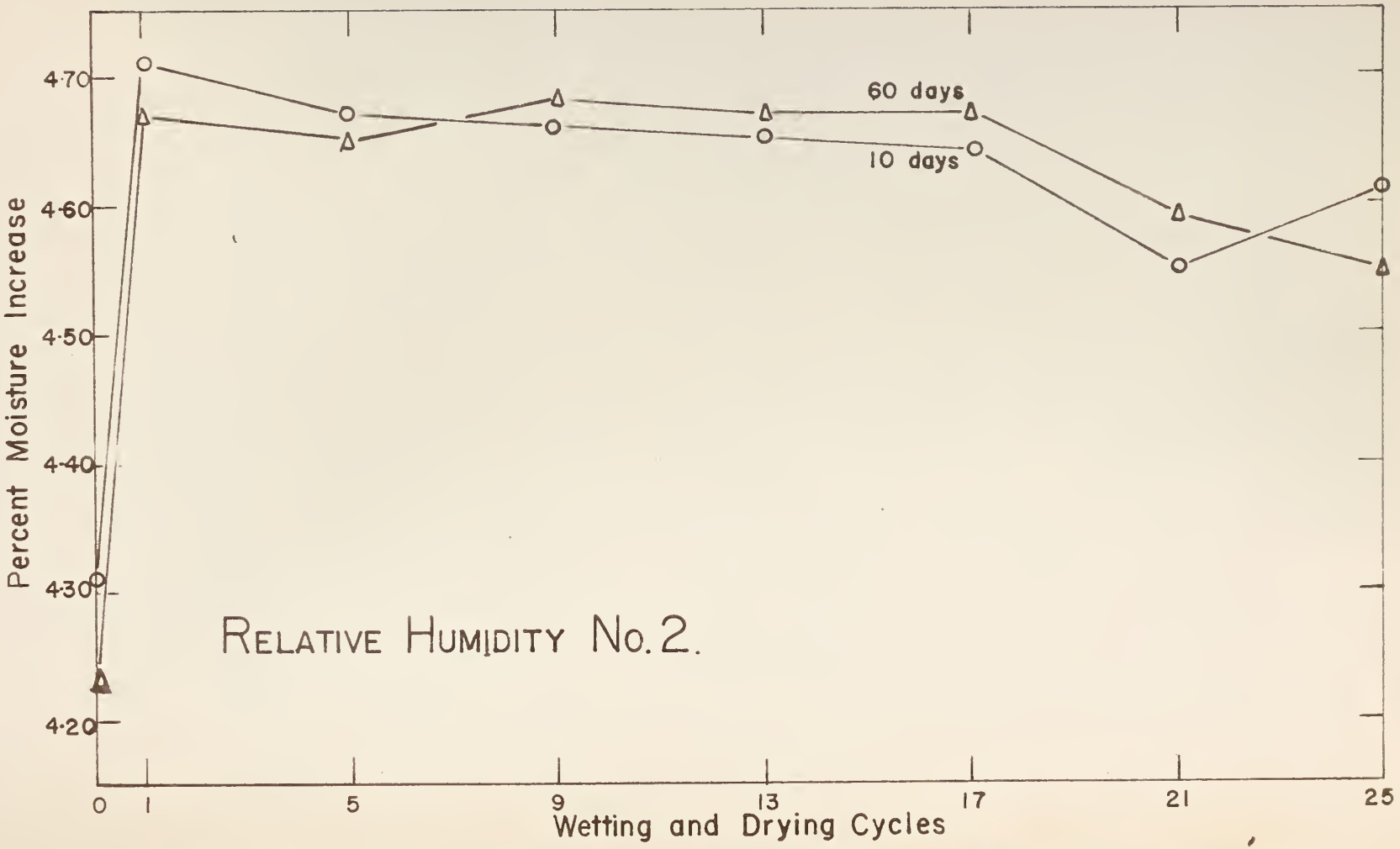


Fig.11 Water Sorption of Dried Linters (Series I). Moisture absorption of a second set of samples from Series I stored in an atmosphere of 45% relative humidity. Confirmation of Fig.10.

in a container which supplied a constant relative humidity of 45% and the uptake of moisture was measured periodically (Table V, Fig.10) until a maximum, and also equilibrium value was reached. To corroborate the results, the sorption experiment was repeated with more Series I sample (Table VI, Fig.11). The data indicates that the two support one another very nicely. In both cases there is a high absorption for sample I-1 as compared to that of the original linters. Columns 6 and 7, Table V, show that the percent water absorbed, based on the original weight of linters samples of Series I employed for water sorption (column 6) is nearly identical to that calculated on the basis of the dry weight of the samples (column 7). The plots in Figures 10 and 11 therefore were all made with values based on the initial weight. When the exposure was of three days duration, Sample I-1 absorbed more than the remaining members of the series (Fig.10). But for the absorption periods of ten days or more, all samples, with the exception of the original linters (1-0) absorbed water to the same extent. The first immersion of cellulose in water followed by sharp drying has apparently the greatest significance in determining accessibility. Furthermore a difference between the samples of Series I in rates of water sorption is indicated - the greatest rate shown again by I-1 and a decreasing rate of absorption paralleling increase in the number of wetting-drying cycles (cf. Fig.10: 3 days, 44 days).

Careful rate determinations should be performed to corroborate this observation since this fact may be of great significance in nitrations carried on for limited times. The larger amount of water absorbed by I-1 over that absorbed by the remaining samples might increase dilution of the acid within the fibers and decrease the extent of nitration of I-1 as compared to say I-25. This increased ease of nitration with increased wetting-drying cycles has been observed by Rosenthal and Brown (3) and is substantiated in this work (Table XII, Fig.16)

The data indicates that the linters which have suffered the greatest "collapse", (measurable by thallation - Fig.12, Table VII), have the greatest potentiality for moisture absorption. Thus the more accessible I-0, and the gradually "expanded" linters from cyclic wetting and drying (I-5 to I-25) have lesser tendency to absorb water, the decreased tendency apparently measuring the extent of collapse. The unusually low absorption for sample I-21 (Figs.10 and 11), the first sample following the accidental heating to 70°C., is interesting. A lower moisture absorption is shown by linters having received six high temperature wettings as compared with linters given only three such wettings (Table V, HT-3). This is probably the same effect which I-21 shows by its decrease in absorption. The apparent drop in the sixty-day value for cycle 25 in Figure 11, like that for cycle 9 in Figure 10, is probably the result of experimental error rather than an inherent phenomena. It might

be noted further that no sorption data was obtained for linters given varied mechanical treatments nor for Series II.

A great many measurements of the accessibility were made with thallous ethylate. This method, while lengthy and prone to error (sometimes 10%), was one which would conveniently measure the accessibility of the linters without further swelling. It was found that the values obtained for any one thallation depended to some extent on uncontrollable factors involved in the preparation of thallous ethylate and the thallation procedure. But by averaging the results (Table VII) for several analyses in triplicate, the trend in accessibility for a series of linters could be established (Fig.12). The high value for the linters I-0 would seem to support the belief that the dewaxed cellulose was in a partially swollen state and that the first wetting and drying brought about the major collapse as measured by the large decrease in the accessibility. Rosenthal reported no accessibility estimation for the original dewaxed linters (46). However the gradual increase in accessibility with additional cycles after the first wetting and drying found in this work agrees very well with Rosenthal's findings. Sample I-21 does not fit into the otherwise smooth curve (Fig.12), showing a slight decrease in ease of penetration by thallous ethylate. This effect is in line with the decreased moisture absorption and probably can be correlated with the higher temperature which inadvertently occurred in cycle 19.

TABLE VII

ACCESSIBILITY OF CYCLICALLY WETTED AND DRIED COTTON LINTERS TO THALLOUS ETHYLATE - SERIES I

Sample No.	Wetting-Drying Cycles	Accessibility in Percent[a] Determination Number 1	2	3	Average
I-0	0	1.65	1.26		1.45
I-1	1	0.43	0.54		0.48
I-5	5	0.63	0.56		0.59
I-9	9	0.67	0.57		0.62
I-13	13	0.84	0.57	0.48	0.63
I-17	17	0.82	0.56	0.56	0.65
I-21	21	0.64	0.67	0.64	0.65
I-25	25	0.87	0.67	0.74	0.76

a. Each figure given, represents the average of three determinations agreeing within ± 10%. Where triplicate determinations did not agree within this margin of error, they were discarded. The majority of results for triplicate determinations agreed to within ± 5% or less.

Linter samples of Series HT which had been given the high temperature wetting (Table VIII, Fig.12) exhibited a gradual decrease in accessibility with repeated wettings, indicating an effect of temperature during swelling of cellulose which appears to confirm the behaviour of sample I-21 mentioned above. Moreover, accessibility for HT-0 was found to be lower than that given by sample I-0. Since neither HT-0 nor I-0 had been wetted, this

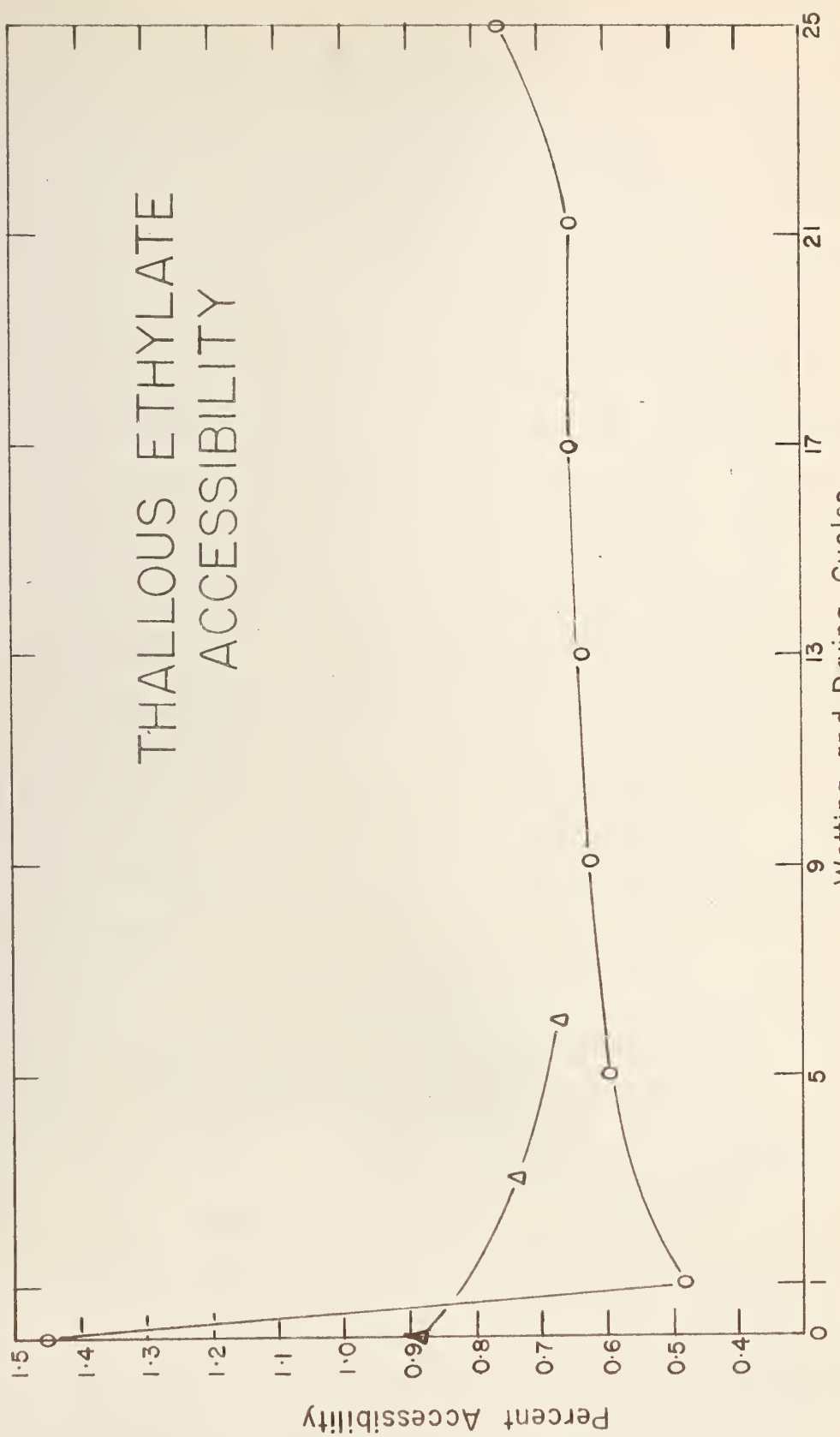


Fig.12 Thallous Ethylate Accessibility.
-O--O- Averaged results from Table VII for the accessibility to thallous ethylate of Series I cotton linters normally wetted and dried.
-Δ--Δ- Accessibility to thallous ethylate of Series HT linters given high temperature wettings.

suggests that the two months greater storage time for HT-0 saw a partial collapse of the "aerogel" obtained from the dewaxing process.

Apparently the mechanical treatment of linters during the wetting and drying is reflected in the accessibility of the product since linters S-IV (Tables IV and IX), differing from S-V in that the latter had not been stirred during immersion, but pressed firmly to remove excess moisture, were found to have a higher accessibility than did S-V. The same phenomenon is found in preparation of paper wherein pressure, applied to the pulp by rollers during drying processes does increase the strength of the paper - presumably by promoting an increased bonding (hydrogen bridges) between cellulose chains. The control samples, S-1, original linters, and S-II, original linters after one cycle, show the expected decrease in accessibility due to wetting and drying of the linters. Since their respective accessibility values are 0.84% and 0.69% and are below those for S-IV and S-V (1.02% and 0.84%), stirring of the linters during the swelling procedure most likely promotes increasing accessibility.

TABLE VIII

ACCESSIBILITY TO THALLOUS ETHYLATE OF LINTERS

CYCLICALLY WETTED AT HIGH TEMPERATURES

Sample	Cycles	Accessibility in Percent#
HT-0	0	0.89
HT-3	3	0.73
HT-6	6	0.67

Each value represents the average of triplicate determinations agreeing within 10%.

TABLE IX

ACCESSIBILITY TO THALLOUS ETHYLATE OF COTTON LINTERS GIVEN SPECIAL WETTING AND DRYING TREATMENTS

Sample	Cycles	Accessibility in Percent#		Average
I-10A	10	2.54		2.54
S-I	0	0.68	1.00	0.84
S-II	1	0.56	0.82	0.69
S-III	1	6.37	4.67	5.52
S-IV	1	1.02		1.02
S-V	1	0.84		0.84
C-1	1	4.03		4.03

Each value represents the average of triplicate determinations agreeing to within 10%. See Table IV for special treatments of these samples.

To obtain an estimate of the degree of swelling found by the tenth wetting (Series I-10), a 5 g. sample of the wet linters was dried by solvent exchange to maintain the water swollen state and stored as I-10A over phosphoric anhydride. The accessibility of I-10A (2.54%) is considerably below that found for S-III (5.52%), which was only wet once and solvent exchange dried, and seems to support the belief of the existence of a partially expanded state in the linters resulting from dewaxing with ethanol-benzene.

Sample C-1 was a diversion from the main problem. It had been observed that filter paper soaked in sodium carbonate and then acidified brought about a great increase in the bulk of the cellulose

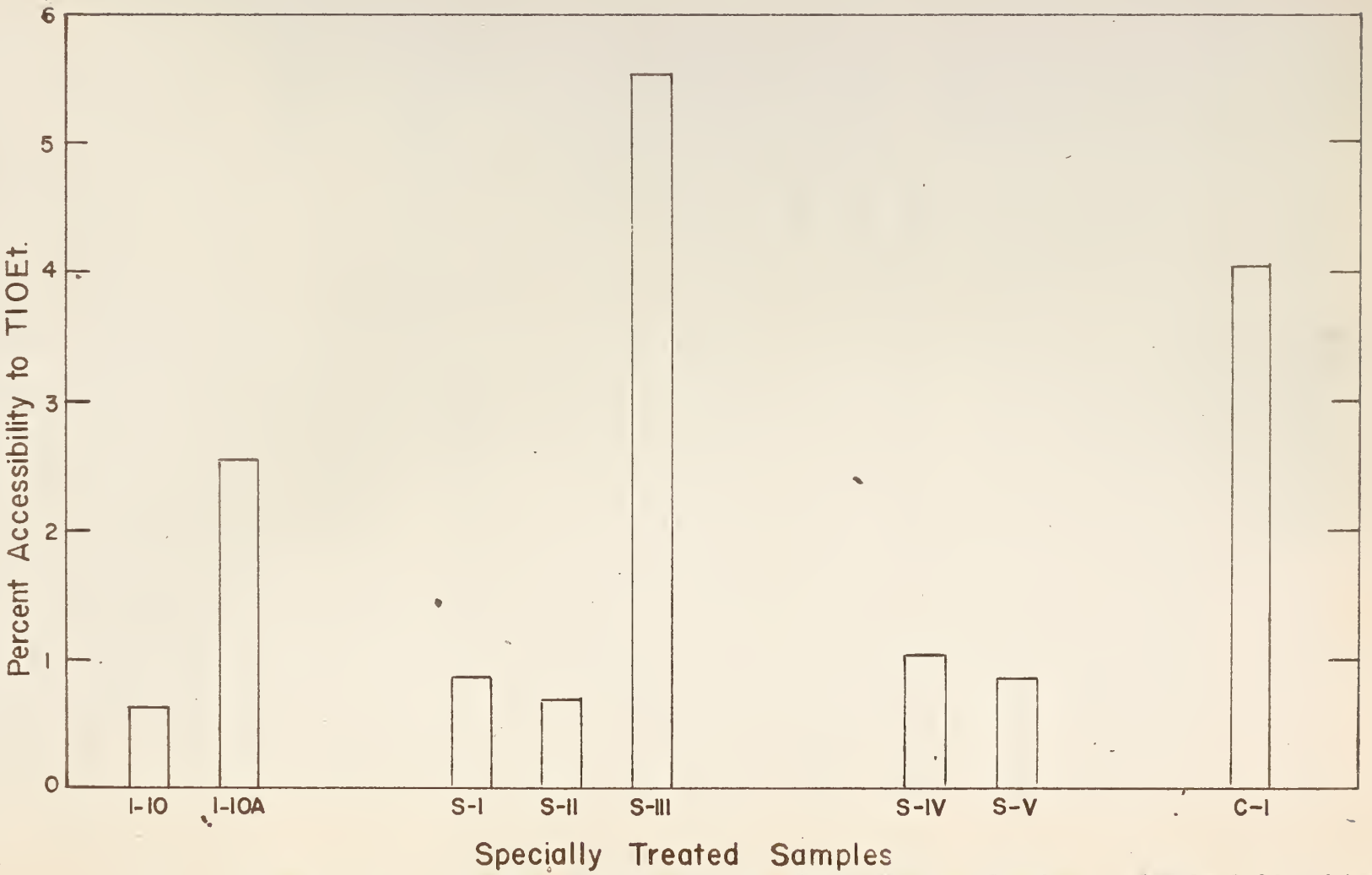


Fig.13 Accessibility to Thallous Ethylate of Specially Treated Samples. Sample 1-10 subjected to 10 cycles. 1-10A is part of 1-10 but solvent exchange dried. s-1 original linters. s-II one normal cycle. s-III part of s-II dried by solvent exchange. s-IV mechanically stirred, then dried. s-V no stirring in wetting, pressed to remove excess moisture. c-1 swollen in 10% sodium carbonate.

as carbon dioxide is produced. A wetting of dewaxed cotton linters under similar conditions was carried out. However, in spite of the apparent swelling, the accessibility to thallous ethylate (4.03%) was somewhat less than that of linters S-III (5.52%) - swollen by ordinary water and dried by solvent exchange. The increase in actual accessibility is more likely due to the swelling effect of the water envelope carried by the sodium ion (73) than due to production of carbon dioxide within the lumen or intermicellar spaces.

Samples from Series I, known to have different accessibilities (Table VII, Fig.12) which had been exposed to a constant relative humidity of 45% were thallated to see if exposure to moisture had a levelling effect on their properties. Table X and Figure 14 show the results obtained. There is a general decrease observed in accessibility for all samples as compared to the values obtained in Series I linters (Table VII, Fig.12). The undulating nature of the resulting curve may possibly be due to an experimental error. Limited size of the samples prevented further thallations to confirm this behaviour.

No thallous ethylate accessibilities have been made on Series II.

Nitration with a standard mixture and analysis for nitrogen content proved a satisfactory method of measuring differences in accessibility. In earlier stages of the investigation, a number of samples from Series I were nitrated (Table XI) at intervals, usually

two samples at a time. This meant that the time the stock solution had stood prior to use was not a constant, a factor which might produce some deviations in results. At first all analyses were carried out by the semi-micro Kjeldahl method (61), but many estimations were useless because of large deviations from the mean value. Better results were obtained by nitrometer analysis of these same nitrated samples, but since several of the nitrated samples shown in Table XI had been stored from some time before analysis by nitrometer, a partial decomposition of the nitrates might have occurred (74).

TABLE X

ACCESSIBILITY TO THALLOUS ETHYLATE OF COTTON LINTERS

SAMPLES OF SERIES I EXPOSED TO CONSTANT RELATIVE HUMIDITY, THEN DRIED

Sample No.	Wetting-Drying Cycles	Average Percent Accessibility[a]
I-0	0	0.67
I-1	1	0.43
I-5	5	0.37
I-9	9	0.47
I-13	13	0.53
I-17	17	0.49[b]
I-21	21	0.44
I-25	25	0.39

a. Determinations were in triplicate.

b. The mean deviation was 0.06, therefore greater than the maximum of 10%. There was insufficient sample to repeat the determination. See Table VI for the moisture sorption for these samples.

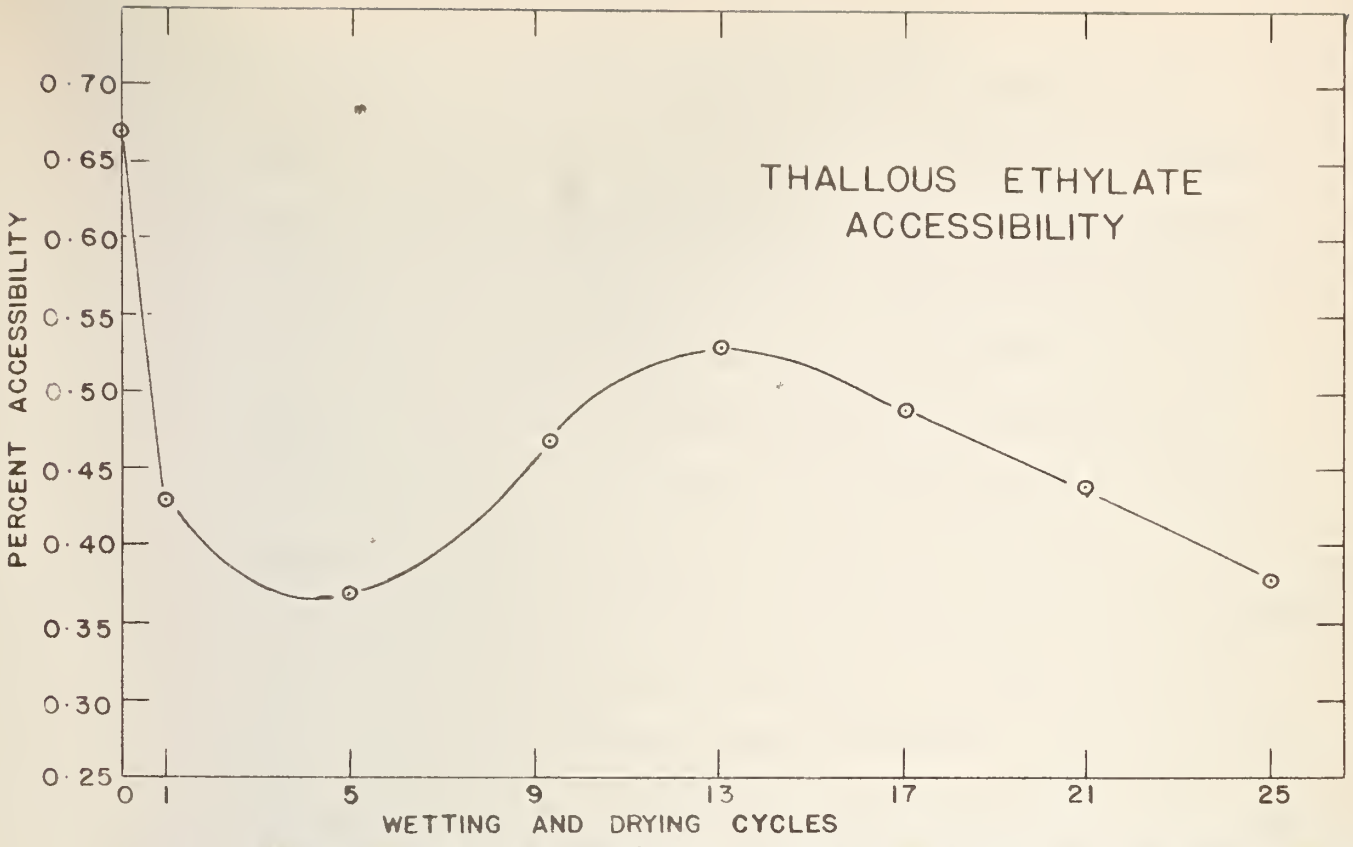


Fig.14 Measurements of accessibility to thallous ethylate of Series I samples after exposure to a 45% relative humidity (Fig.10)

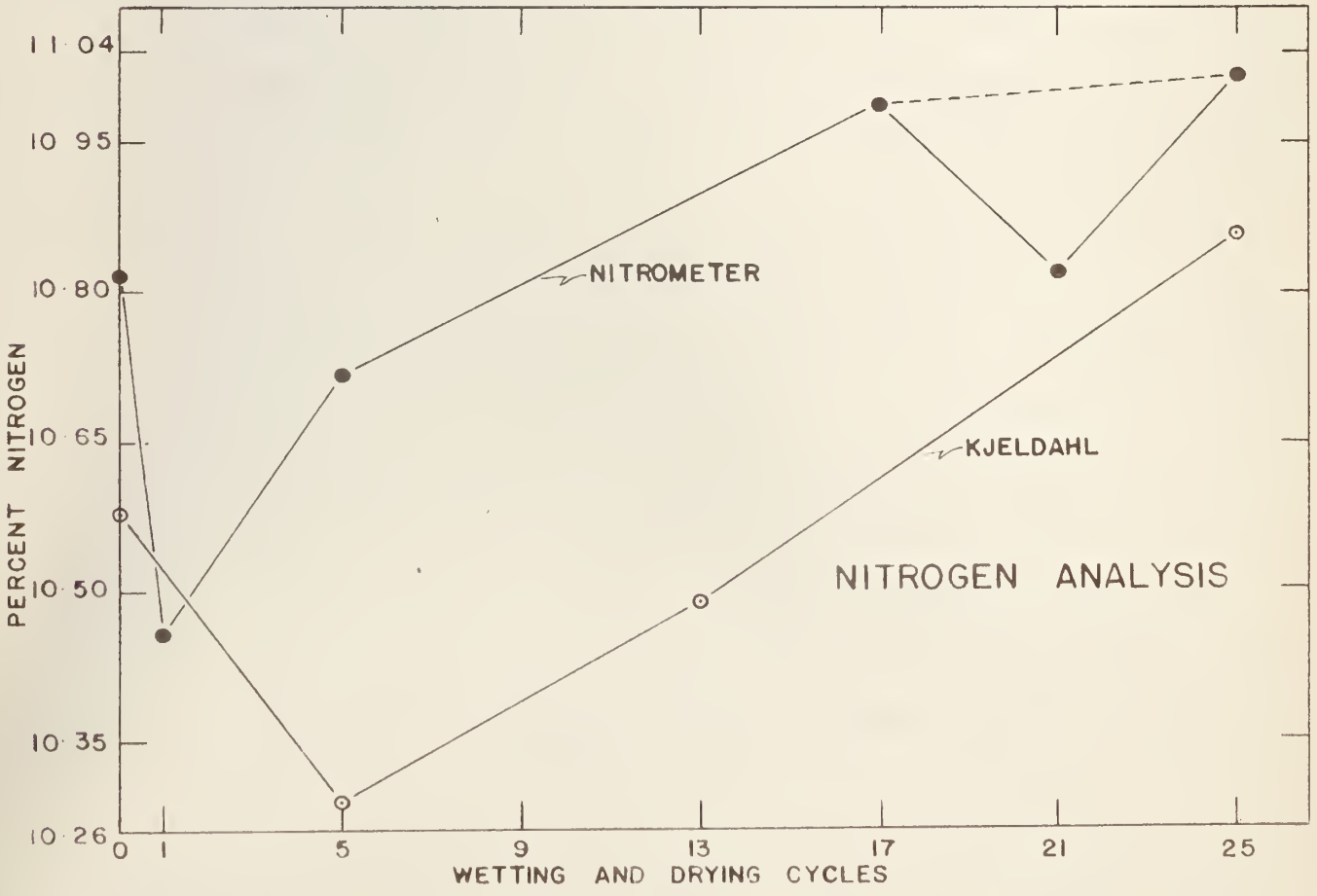


Fig.15 Nitrogen content of Series I samples nitrated and analysed at different times by both Kjeldahl and nitrometer methods.

This may account for the somewhat irregular results shown in Table XI and Figure 15. In order that results could be obtained which would compare more favorably, nitration of all the samples of Series I was carried out in one day using identical conditions. All nitrogen analyses (Table XII) were then carried out in the same day. The amount of moisture absorbed by the samples was calculated, and the results were all corrected for this moisture absorption. This was found to be necessary since the partially nitrated linters rapidly absorbed water during weighing - a property which would give unusually low values for nitrogen content for those samples which absorbed water more readily. Furthermore, the small differences in nitrogen values which reflect the differences in accessibilities would therefore be overshadowed by experimental errors. A set of samples from Series II was treated in exactly the same manner and analysed similarly with the nitrometer (Table XIII). The results of the two series show the same general trend (Fig.16), an increase of ease of nitration with number of wetting-drying cycles. The difference in the nitrogen contents of the original linters samples I-0 and II-0 is interesting and also somewhat large to be accounted for by experimental error since the nitrometer gives good reproducibility in analysis. The thallous ethylate accessibility value for accessibility of I-0 should be greater than that for II-0 (p.71 cf. HT-0 and I-0) since the dewaxed linters for Series II had been stored for one year, which would permit a collapse of the partially swollen "aerogel". Accordingly the

nitrogen content should be greater for I-0 than for II-0, yet the reverse is found (I-0, 10.70%; II-0, 10.96%), and in general all the nitrated samples of Series II are about 0.2 to 0.3% higher in nitrogen content than those for Series I. This may be the

TABLE XI

NITROGEN CONTENT OF THE NITRATES OF COTTON LINTERS WHICH HAD BEEN CYCLICALLY WETTED AND DRIED - SERIES I

Sample No.	Wetting-Drying Cycles	Percent Nitrogen Kjeldahl Nitrogens[b]	Nitrometer Nitrogens[c]
I-0	0	10.58 (9 detns)	10.82 (6 detns)
I-1	1		10.46 (4 detns)
I-5	5	10.29 (7 detns)	10.72 (4 detns)
I-13	13	10.49 (11 detns)	
I-17	17		10.99 (4 detns)
I-21	21		10.82 (4 detns)
I-25	25	10.86 (6 detns)	11.02 (5 detns)

a. Although these nitrations employed the same nitration mixture, they were carried out at times up to a month apart. Storage time for the nitrate before analysis varied from sample to sample.

b. Kjeldahl determinations were found to have larger deviations than those found in nitrometer analyses.

c. Nitrometer results deviated less than ± 0.05%.

TABLE XII

NITROGEN CONTENT OF THE NITRATES OF COTTON LINTERS WHICH HAD BEEN CYCLICALLY WETTED AND DRIED - SERIES I

Sample No.	Wetting-Drying Cycles	Percent Nitrogen (nitrometer)
I-0	0	10.70
I-1	1	10.70
I-5	5	10.70
I-9	9	10.88
I-13	13	10.91
I-17	17	10.86
I-21	21	10.96
I-25	25	10.97

a. Nitrations were all carried out the same day with the same nitration mixture. After storage under vacuum over phosphoric anhydride for one week, samples were weighed and then allowed to absorb moisture to come to equilibrium with room conditions, then re-weighed. Corrections were made for absorbed moisture and samples were all analysed at the same time. Results are averages of two or three determinations. Maximum deviations are less than 0.5% of the nitrogen percent.

TABLE XIII

NITROGEN CONTENT OF THE NITRATES[a] OF COTTON LINTERS WHICH HAD BEEN CYCLICALLY WETTED AND DRIED - SERIES II

Sample No.	Wetting-Drying Cycles	Percent Nitrogen[b] (nitrometer)
II-0	0	10.96
II-1	1	10.93
II-5	5	10.95
II-9	9	10.97
II-13	13	10.99
II-17	17	11.01
II-21	21	11.04
II-25	25	11.09

a. Samples were all nitrated on the same day approximately two weeks after nitration of Series I, using the same nitration mixture under identical conditions.

b. All percents shown are the averages of two determinations agreeing to less than 1% error. Sample II-9 is an average of four determinations.

result of Series I having been stored for nearly thirteen months, i.e. it had been standing so long that it suffered a partial collapse of accessibility, and this may account for some of the irregularities in the plot for Series I (Fig.16). Series II, while it has a smaller overall increase in nitrogen content than shown by Series I, yields a smooth curve with the exception of a small drop from original linters to those which had been once wetted and dried. An important conclusion which can be made is that even with the number of wetting-drying cycles made, a maximum nitration has not been obtained, and since nitration is an equilibrium reaction, this equilibrium has therefore not been reached under the conditions used. An extended nitration period should provide the attainment of equilibrium if the differences in nitration can be attributed to differences in accessibility - a matter which is physical in nature rather than chemical. The results of an experiment in which nitration time has been extended from one-half hour to one and one-half hours (Table XIV) show that within the limits of experimental error, these differences have been eliminated and a maximum value of 11.27% nitrogen for all samples, regardless of accessibility.

Samples which had been exposed to atmospheric conditions were nitrated at the same time as were those of Series II and under the same conditions. Table XV shows that these Series I samples which had been exposed to the atmosphere did not all show the same extent of nitration as had been expected (75), but rather exhibited

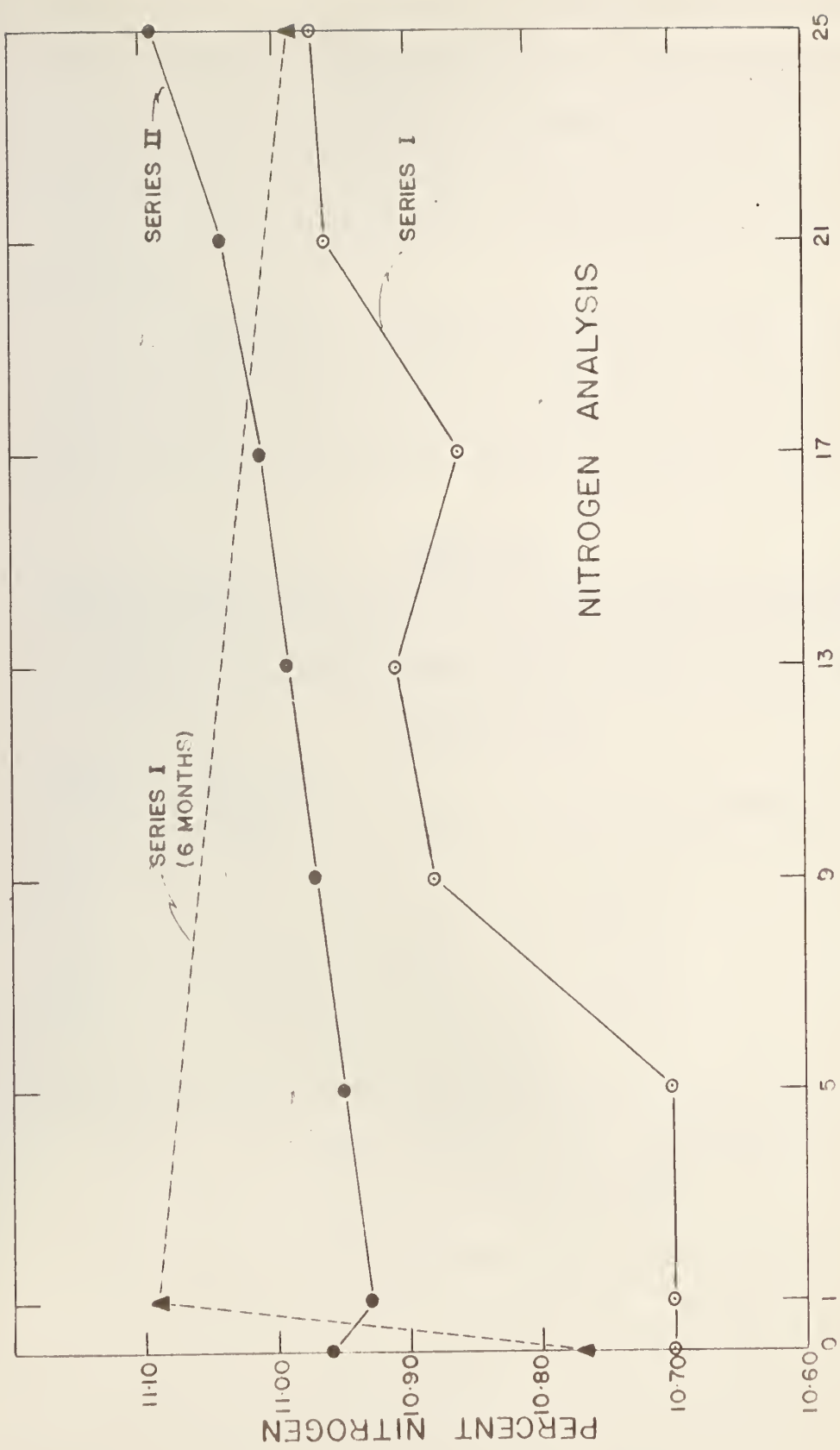


Fig.16 Nitrogen Analyses. Series I and Series II samples nitrated and analysed under comparable conditions. Series I samples which had been exposed to atmospheric conditions for six months are compared.

a large increase in the accessibility of the sample wetted and dried once (Fig.16). The other two samples analysed showed but small differences from the results for the same samples which had not been exposed (Table XII). The number of samples analysed is too small to give the plot significance, but the similarity to the moisture absorption curve, from a constant humidity (Fig.10), is remarkable.

Heavy water exchange with its resulting high accessibility values appeared to be a promising method of measuring the differences brought about by cyclic wetting and drying of the linters.

TABLE XIV

NITROGEN CONTENT FROM NITRATION[a] OF COTTON LINTERS WHICH HAD BEEN CYCLICALLY WETTED AND DRIED, THEN NITRATED FOR AN EXTENDED NITRATION PERIOD

Sample No.	Wetting-Drying Cycles	Percent Nitrogen[b] (nitrometer)
I-0	0	11.25
I-1	1	11.29
I-25	25	11.27

a. Nitration period was for ninety minutes, three times the length of the normal nitration. The same nitration mixture was used as for other nitrations reported.

b. Average of two determinations.

TABLE XV

NITROGEN CONTENT FROM NITRATION OF COTTON LINTERS WHICH HAD BEEN CYCLICALLY WETTED AND DRIED, THEN STORED AT ROOM CONDITIONS FOR SIX MONTHS PRIOR TO NITRATION

Samples were dried over phosphoric anhydride prior to nitration under identical conditions.

Sample No.	Wetting-Drying Cycles	Percent Nitrogen (nitrometer)
I-0	0	10.77[a]
I-1	1	11.09[a]
I-25	25	10.99[b]

a. Average of three determinations.

b. Average of two determinations.

The technique outlined by Mark, et al. (4, 63), was followed and the empirical value F, was calculated for Series I (Table XVI) and Series II (Table XVII). The reactions go almost to completion (Figs. 17 and 19) within the first half hour, so this is the important part of the curve. In order to evaluate the results on a comparative basis, the rates of exchange were compared at a half hour and at one hour for each sample (Figs. 18 and 20). Since these results (Figs. 18 and 20) represent only one exchange for each sample of a series, and the differences measured in specific gravity are of the order of 4×10^{-4}, the chance of error is fairly high. However the results seem to follow the general pattern established by thallation and nitration and show an increase in

the accessibility for increased numbers of wetting and drying cycles. Further work is planned for the immediate future using this technique.

TABLE XVI

HEAVY WATER EXCHANGE MEASUREMENTS OF ACCESSIBILITY OF CELLULOSE

SERIES I

Sample No.	Values of F^a at Reaction Times (hours) 0	0.5	1.0	4.0	24.0
I-0	0	0.26	0.38	0.51	0.44
I-1	0	0.25	0.27	0.47	0.44
I-5	0	0.34	0.40	0.45	0.48
I-17	0	0.37	0.40	0.39	0.42
I-21	0	0.50	0.43	0.52	0.52
I-25	0	0.46	0.51	0.34	0.48

a. The empirical quantity F was calculated from measured changes in the specific gravity.

TABLE XVII

HEAVY WATER EXCHANGE MEASUREMENTS OF ACCESSIBILITY OF CELLULOSE

SERIES II

Sample No.	Values of F^a at Reaction Times (hours) 0	0.5	1.0	1.5	2.0	3.0	4.0
II-0	0	0.26	0.30	0.32	0.46	0.39	0.33
II-1	0	0.37	0.37	0.38	0.40	0.38	---
II-5	0	0.32	0.35	0.30	0.38	0.41	0.30
II-17	0	0.33	0.36	0.32	0.34	0.35	0.38
II-21	0	0.33	0.32	0.30	0.38	0.46	0.31
II-25	0	0.37	0.38	0.41	0.38	0.40	0.40

a. The empirical quantity F was calculated from measured changes in the specific gravity.

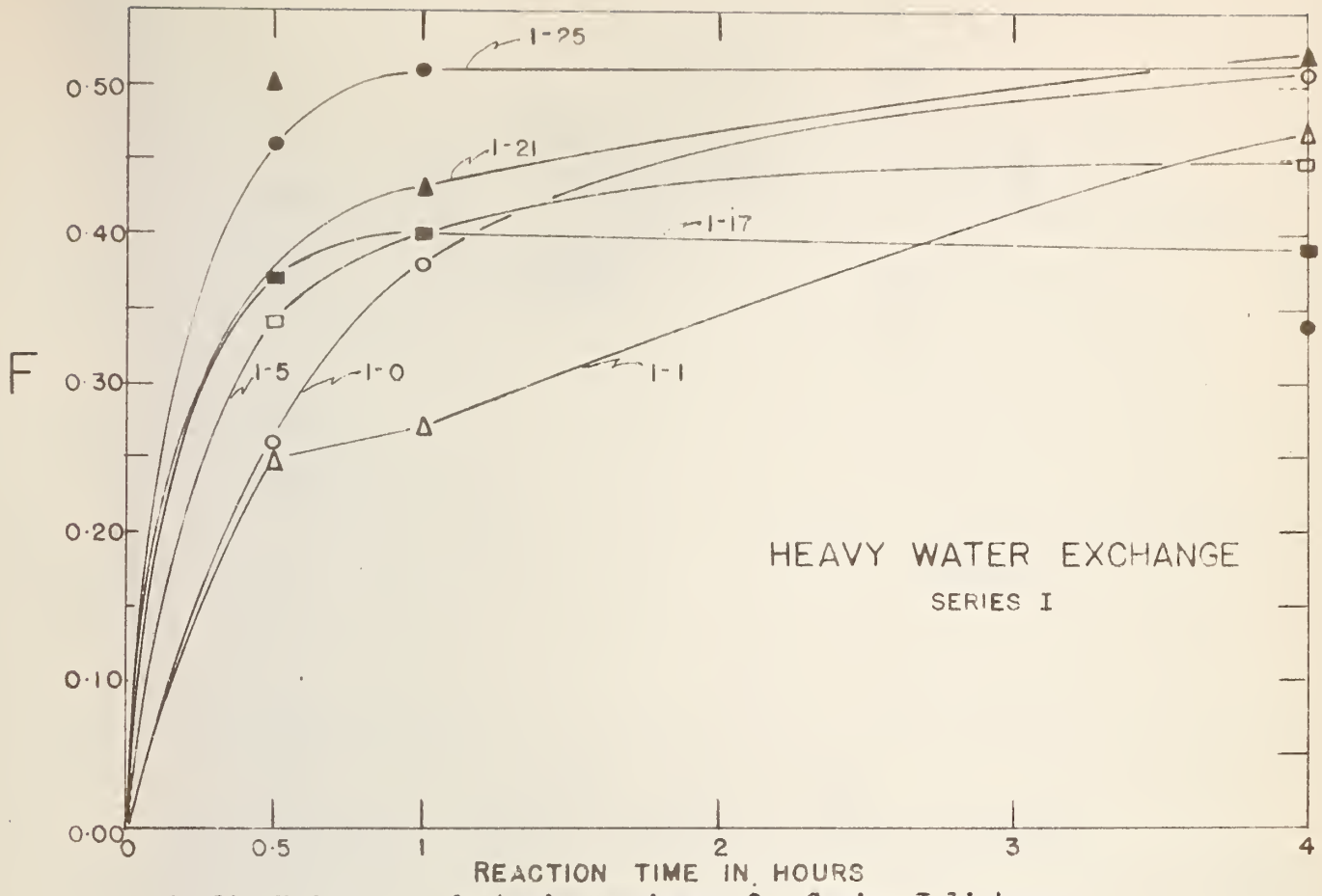


Fig.17 Hydrogen - deuterium exchange for Series I linters.

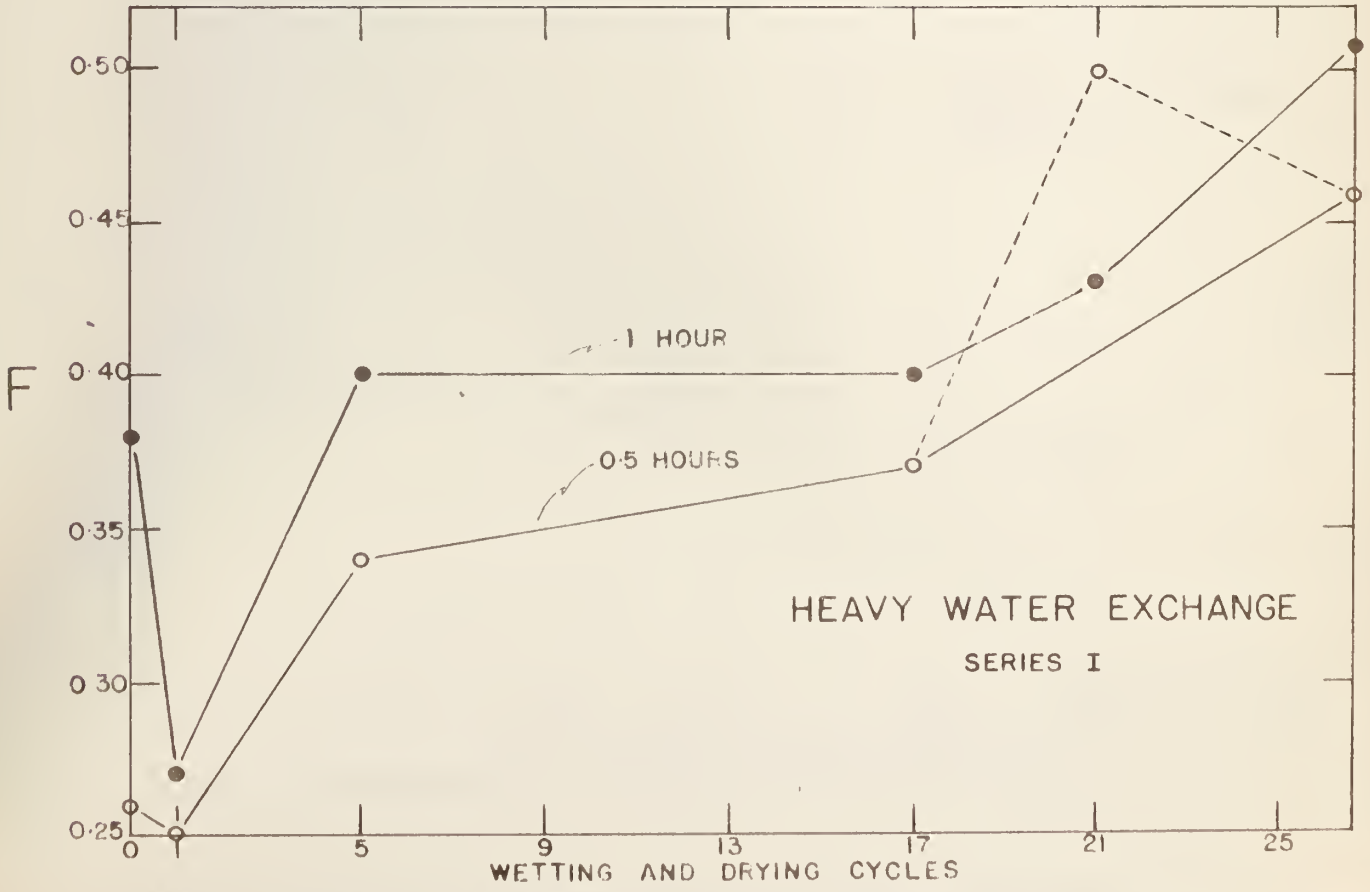


Fig.18 Hydrogen - deuterium exchange for Series I linters

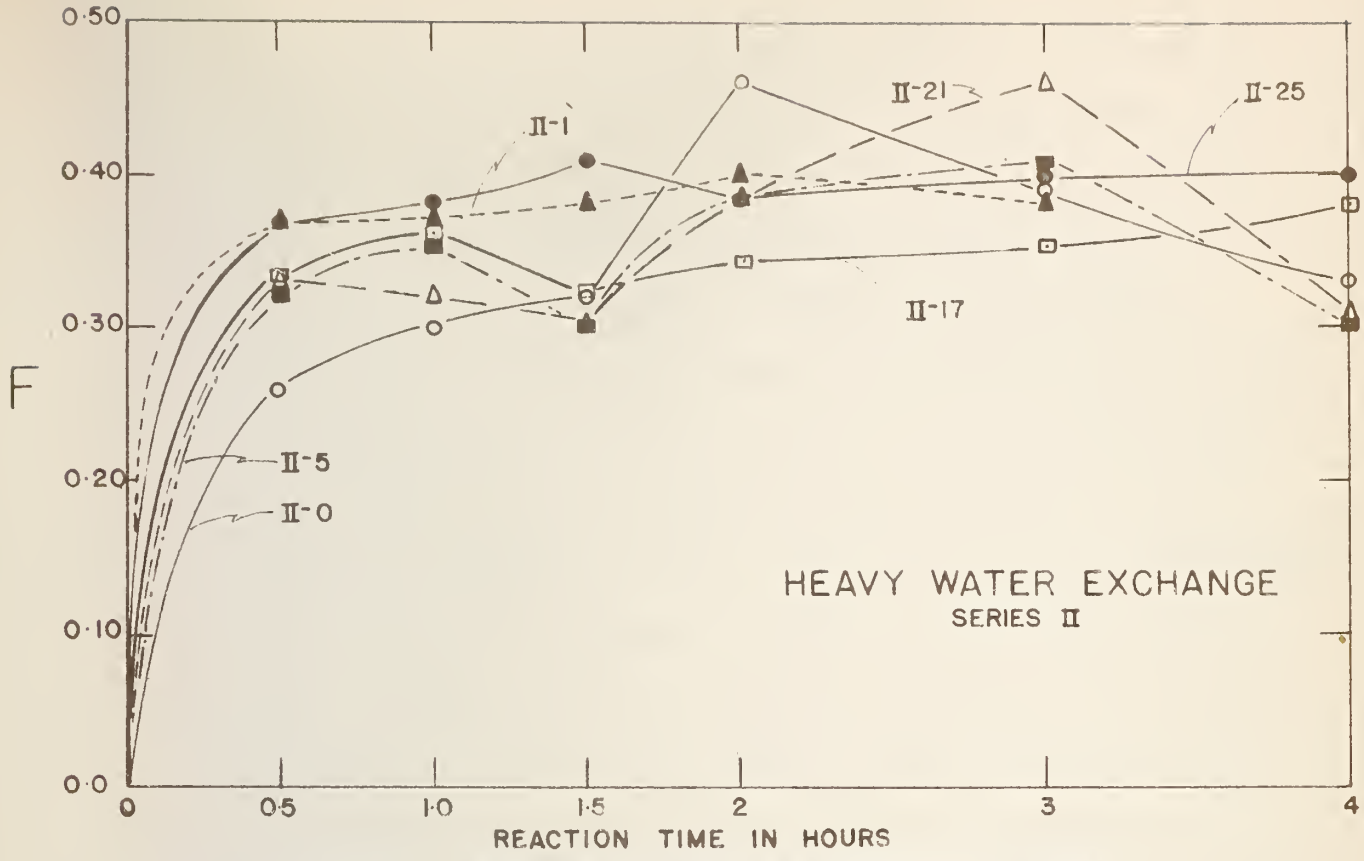


Fig.19 Hydrogen - deuterium exchange for Series II linters.

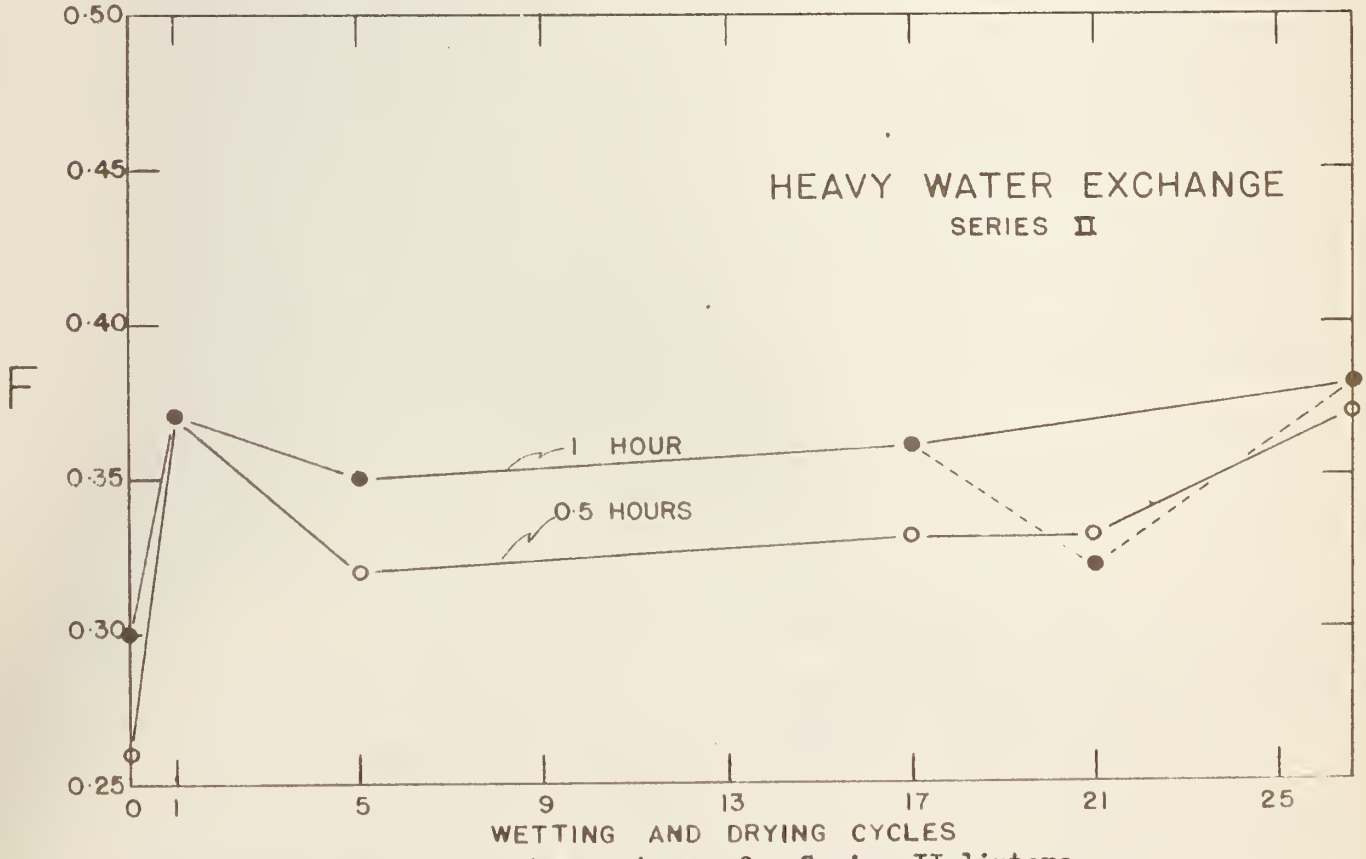


Fig.20 Hydrogen-deuterium exchange for Series II linters.

For the purpose of obtaining an overall picture of the changes in reactivity of cellulose which have been brought about by cyclic wetting and drying, a composite graph (Fig.21) has been drawn. Different scales are necessary in order to accumulate the results on one graph. There is a gradual increase in the accessibility to nitration, thallation and deuterium exchange, with a corresponding increase in the number of alternate wetting and drying cycles to which the sample has been subjected. But the differences in numerical values lends support to the statement that the term "accessibility" must be coupled with the particular reagent involved before it has definite meaning (37). The initial decrease in the accessibility between original linters and those having been wetted and dried once is repeated by each set of analyses, but only the thallation technique shows lower accessibility to the reagent for all samples from one to twenty-five cycles than for the original dewaxed linters. Moisture absorption results are in direct contrast to the results of the other three methods - a high absorption for sample I-1 followed by decreasing absorptive powers for the following samples of the series. If the amount of absorption can be taken as a measure of the collapsed state, assuming that a greater degree of absorption is possible when collapsed, the absorption results would appear to agree very well with the other methods of determination.

This, and previous investigations, have shown that moisture history as well as temperature play important roles in the properties of cellulose. Since irregularities occur in the burning qualities of

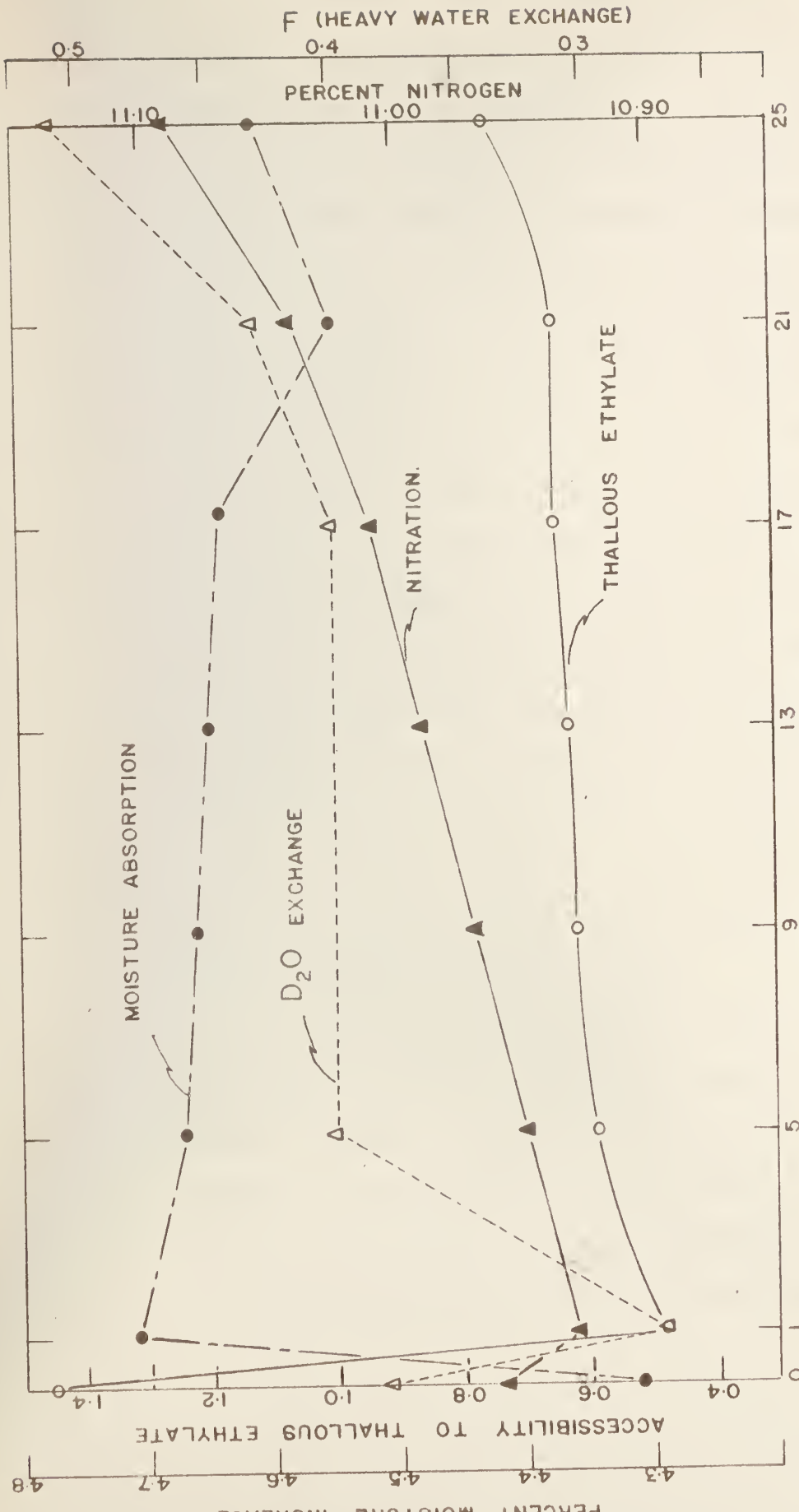


Fig.21 Comparison of the different methods used in measuring changes brought about in the accessibility of cellulose to reagents.
-O--O- Thallous ethylate curve (Fig.10) for Series I.
-▲--▲- Nitration curve for Series II (Fig.14).
-Δ--Δ- Heavy water exchange measurement at one hour for Series I (Fig.19)
-●--●- Moisture absorption at 45% relative humidity after ten days for Series I (Fig.17)

nitrated pulps from different sources (1), there exists the possibility that growing conditions in different localities might promote differences in accessibilities of the cellulose. Microscopic studies of the growth of cotton hairs have shown that following normal growth, a ring appeared in cross-section for each day during the growing period. When uniform conditions of temperature, humidity and light were used continuously day and night, these rings did not appear (68). Similarly it is known that growth rings in trees reflect seasonal changes, i.e. in poor conditions such as drought, the cells are closely packed in growth, while in moist warm weather they are formed as large cells in a more loosely arranged state. It should not be unreasonable to expect a lower accessibility to reagents (and higher crystallinity) in the more closely packed cell structure, hence pulp taken from an area with conditions promoting growth of a larger ratio of closely packed cell structures would be expected to have an overall lower accessibility to reagents. It has not been possible to obtain data to check this suggestion, but the evaluation of the climatic factor should prove a worthwhile problem.

Furthermore, an interesting problem for investigation has arisen from the studies of the heats of adsorption carried out by Morrison, Campbell, and Maass, in which they describe a heat of adsorption of cellulose which had been first mercerized with the same strength alkali solution, as greater than that found for ordinary unmercerized linters (69). This additional energy released was

termed "heat of mercerization", and was found to be proportionally larger for increased concentrations of alkali used. Since alkali solutions are known to have marked swelling properties (76) the treatment given might be in effect, equivalent to several wettings. The "heat of mercerization" could thus be a measure of accessibility. Preparations are under way to measure heats of wetting of samples of Series I and II to see if the "heat of mercerization" may not be used as an analytical tool to measure increase in accessibility.

SUMMARY

Dewaxed cotton linters were alternately wetted with distilled water at room temperature and dried over phosphoric anhydride under vacuum for twenty-five successive cycles. A second series of samples was similarly processed to confirm the results of the first. More dewaxed cotton linters were exposed to immersions at approximately 80°C., and then dried over phosphoric anhydride, up to a maximum of six cycles.

Analyses for changes in the accessibility of the linters in their dry state were carried out using a thallation and methylation technique on selected samples representative of different stages in the normal cyclic wetting and drying treatment. It was found that while there was an initial drop of the accessibility to thallous ethylate with the first wetting and subsequent drying, the successive wetting and drying cycles tended to show an increase in degree of thallation which appeared to parallel the increase in the number of cycles to which the samples had been subjected. In contrast to the results for room temperature wetting, the high temperature immersions continued to show a decreasing accessibility with successive wetting and drying. The original linters for the high temperature series did not exhibit as high an accessibility to thallous ethylate as was the case for the room temperature series, but after six successive high temperature cycles the accessibility of the linters was still above that for a single wetting and drying at normal temperatures. There are indications that this was a function of the original linters.

Nitration of samples which had been wetted and dried at room temperature yielded nitrates of progressively higher nitrogen

content paralleling the number of cycles to which the samples had been subjected. The difference found between the selected samples of the series was eliminated when the nitration was extended from the usual one-half hour period to one and one-half hours. The nitrogen value in this case was also higher than that for the one-half hour nitrated samples indicating that in the shorter reaction time, attainment of equilibrium was incomplete and could be controlled in some measure by the physical state of the linters.

The deuterium - hydrogen exchange method of measuring accessibility was attempted and the results supported the previous observations that the accessibility of the linters increases with additional wetting and drying cycles.

The degree of dispersion of the cotton fibers was found to have a small effect on the accessibility to thallous ethylate. Fibers dispersed by stirring during the distilled water immersion and drained free of excess water with no pressure applied to compress the fibers, were found to have a slightly higher accessibility than fibers which were not stirred during immersion and were subsequently pressed firmly to remove excess water.

The foregoing results strongly indicate that the previous moisture history of cellulose determines in part the accessibility variations which are encountered in the manufacture of cellulose derivatives.

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